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THE IN-PLACE POLLUTANTS PROGRAM

VOLUME III

PHASE 1 STUDIES

October, 1987

Ministry
of the
Environment

Ontario

J. Bishop, Director
Water Resources Branch

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PREFACE

The In-Place Pollutants Program addresses the impact of contaminants in sediment on overlying water quality and aquatic biota with the aim of developing strategies for the management of contaminated sediments.

This report, Volume III, describes the field and laboratory studies carried out in the Phase 1 studies and discusses the findings. Companion volumes will provide the following:

Volume I - A Program Overview (Feb. 1987)

Volume II - Background and Theoretical Concepts (Feb. 1987)

Volume IV - Phase 1 Data Summary (Oct. 1987)

Subsequent phases of the In-Place Pollutants studies will be reported in other volumes of this series.

The In-Place Pollutants Program of the Ministry of the Environment is supported in part by funds received from Environment Canada under terms of the Canada-Ontario Agreement (COA) on Great Lakes Water Quality. Activities are co-ordinated with those of the Federal government under guidance of the COA Contaminated Sediments Committee.

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SUMMARY

This report documents the studies and findings associated with the first phase of the In-Place Pollutants Program. The study addressed contaminant levels in sediments and benthic organisms from 12 locations in Lake Ontario and the Great Lakes Interconnecting Channels. The main objectives of the study were threefold:

1. To determine the spatial distribution of selected contaminants in sediment and establish the factors influencing such distribution.

2. To determine the biological and physico-chemical availability of heavy metals from sediment.

3. To determine the levels of various contaminants in benthic organisms and the relationship of these levels to those in the sediment that the organisms feed on.

The findings of the Phase 1 studies are summarized below:

SEDIMENT

General

Considerable variations in sediment type and chemistry were noted within and among the different locations sampled.

The contaminants were associated mainly with the fine-grained (silts and clays) fraction of sediment, especially the organic matter in the fine sediment fraction. The organic component (measured as loss on ignition (LOI), total organic carbon (TOC), total Kjeldahl nitrogen (TKN), and solvent extractables (SOL)), was the major factor influencing the distribution of contaminants in sediments.

Pesticides, in general, were found at low concentrations in sediments although there appear to be constant low level discharges of these from urban storm sewers and sewage treatment plant outfalls. It appears that once the pesticides become associated with the predominantly anaerobic sediments they are readily degraded.

Lake Locations

Among the Lake Ontario locations, Windermere Basin (in Hamilton Harbour) had the most contaminated sediments followed by Toronto Harbour and Humber Bay.

High organic enrichment (LOI, TOC, SOL, TKN) was noted in Frenchman Bay and Windermere Basin. In Frenchman Bay, the enrichment appears to be due mainly to the naturally occurring peat-like substrate whereas in Windermere Basin, the enrichment appears to be due mainly to industrial material such as solvent extractables (oils and greases).

Unusually high levels of chromium were noted in Windermere Basin, Humber Bay and Toronto Harbour. This appears to be a reflection of high uses of this metal in these urban areas.

The Toronto East Headland appears to be the major source of contaminants to local sediments (around the headland), including the outer harbour.

River Locations

St. Marys River was the most contaminated of the river locations showing high levels of zinc, lead, copper, manganese, iron, chromium and solvent extractables. Most of these parameters can be attributed to discharges of metal processing (steel manufacture) wastes to the river.

The highest levels of mercury were noted in the St. Clair and Niagara Rivers.

With the exception of St. Marys River and mercury in the St. Clair and Niagara Rivers, the sediments of the interconnecting channels were relatively clean, approximating those of the Eastern Toronto Waterfront which had the cleanest sediments among all locations sampled.

BENTHIC ORGANISMS

The benthic populations in many of the areas sampled were reduced to two species of oligochaetes (*T. tubifex* and *Limnodrilus hoffmeisteri*). These two species appear to be more tolerant of high levels of contamination such as exist in Toronto Harbour and Humber Bay.

At some stations with heavily contaminated sediments such as Windermere Basin and St. Marys River, there appeared to be a toxic influence on biota. Although the sediment provided a suitable physical substrate, it was devoid of organisms.

The sediments at two stations in the upper St. Marys River (above the industrial discharges), one station in the St. Clair River and three stations in the St. Lawrence River had an abundance of "clean-water" benthic organisms.

Two trends in contaminant uptake were noted:

(a) Pesticides, which were measured at low concentrations in sediments were elevated in benthic tissue in the vicinity of storm sewer outfalls and sewage treatment plant discharges. Based on other MOE studies, it appears that these pesticides are discharged at low concentrations from these outfalls and are taken up by the benthic organisms in the vicinity of the discharges. Once in contact with the predominantly anaerobic sediments the pesticides are degraded within a relatively short period of time.

(b) Mercury, PCBs, copper and zinc were accumulated by the benthos from sediments. The uptake of these parameters is influenced by the organic matter content of the sediment, especially the solvent extractables (oils and greases). In areas with high levels of organic matter, uptake was very low although the levels of Cu, Zn, Hg and PCB's were generally at their highest in sediment. In contrast, the highest uptake occurred in sediments with low organic matter content.

The zinc and copper levels in organisms were not related to the total levels of these metals in sediments but appeared to be related to specific geochemical fractions. For zinc the F4 phase (moderately reducible fractions associated with iron and manganese carrier particles) was the major source to biota whereas for copper, the F3 phase (organic/sulphide) had the major influence.

CONCLUSIONS

Evidence strongly suggests that contaminated sediments are sources of contaminants to benthic organisms and can exert toxic influences on benthic organisms by completely eliminating their survival or reducing the diversity to a few tolerant species. The survival of benthic organisms in polluted sediments and the concentration of certain contaminants in the tissues of these organisms raise concerns related to the potential for transfer of these contaminants to organisms higher in the food chain.

The effects of continuing discharges such as storm sewers and sewage treatment plant discharges cannot be overlooked, since they are still of major concern in areas with contaminated sediments. Any management strategy to improve sediment quality must first address the input from these sources.

SOMMAIRE

Le présent rapport étaie les études et les conclusions concernant la première phase du Programme d'étude des sédiments contaminés. L'étude a porté sur la teneur en contaminants des sédiments et des organismes benthiques de 12 points du lac Ontario et des voies d'eau de communication des Grands Lacs. Les objectifs principaux de l'étude couvraient trois domaines :

1. Détermination de la distribution spatiale de certains polluants dans les sédiments et recherche des facteurs influant sur cette distribution.

2. Détermination de la présence biologique et physico-chimique des métaux lourds dans les sédiments.

3. Détermination des concentrations de divers polluants dans les organismes benthiques et rapport entre ces concentrations et celles relevées dans les sédiments dont se nourrissent ces organismes.

Nous résumons ci-dessous les conclusions des études de la phase 1 :

SÉDIMENT

Généralités

On a remarqué d'importantes variations dans le type et la chimie des sédiments, dans les différents points échantillonnés et entre eux.

Les polluants se rattachaient essentiellement à la partie fine (limons et argiles) des sédiments, en particulier la matière organique dans la partie de sédiments fins. Le composant organique (déterminé d'après la perte au feu ‹PAF›, le carbone organique total ‹COT›, l'azote Kjeldahl total ‹AKT› et les composés extractibles solvants ‹CES›) a été le facteur principal agissant sur la distribution des polluants dans les sédiments.

En général, on a rencontré des pesticides en faibles concentrations dans les sédiments, mais il semble en exister un faible apport constant venant des déversements des égouts pluviaux urbains et des stations de traitement des eaux usées. Il semble que les pesticides se décomposent facilement après leur association aux sédiments à prédominance anaérobique.

Points du lac étudiés

Parmi les points du lac Ontario, le bassin de Windermere (dans le port d'Hamilton) possédait les sédiments les plus contaminés, suivi du port de Toronto et de la baie de la rivière Humber.

On a remarqué un fort enrichissement organique (PAF, COT, CES et AKT) dans la baie Frenchman et le bassin de Windermere. Dans la baie Frenchman, l'enrichissement paraît provenir essentiellement d'un substrat tourbeux naturel, alors que dans le bassin de Windermere, il proviendrait surtout de matières industrielles comme les composés extractibles solvants (huiles et graisses).

On a relevé des niveaux anormalement élevés de chrome dans le bassin de Windermere, la baie Humber et le port de Toronto, ce qui s'expliquerait par l'utilisation intense de ce métal dans ces zones urbaines.

Le promontoire de Toronto Est semble être la source essentielle de polluants dans les sédiments locaux (au voisinage du promontoire), y compris le port extérieur.

Points en rivière

La St. Marys était la plus contaminée des rivières, avec des niveaux élevés des élements suivants : zinc, plomb, cuivre, manganèse, fer, chrome et composés extractibles solvants. On peut attribuer la plupart de ces paramètres au rejet de déchets de traitement des métaux (sidérurgie) dans la rivière.

On a noté les concentrations les plus élevées de mercure dans les rivières St. Clair et Niagara.

À l'exception de la rivière St. Marys et du mercure dans les rivières St. Clair et Niagara, les sédiments des voies d'eau de communication étaient relativement propres, approximativement analogues à ceux du littoral de l'est de Toronto, qui possède les sédiments les plus propres de tous les points échantillonnés.

Organismes benthiques

Dans la plupart des zones échantillonnées, les populations benthiques se réduisaient à deux espèces d'oligochètes (T. tubifex et Limnodrilus hoffmeisteri). Ces deux espèces semblent tolérer le mieux les concentrations élevées de pollution présentes dans le port de Toronto et la baie Humber.

En certains points ayant des sédiments fortement pollués, comme le bassin de Windermere et la rivière St. Marys, le biotope semble subir une influence néfaste. Les sédiments représentent un substrat physique suffisant, ils sont néanmoins dépourvus d'organismes.

Les sédiments en deux points en amont de la rivière St. Marys (au-dessus des rejets industriels), en un point de la rivière St. Clair et en trois points du St-Laurent présentaient une abondance d'organismes benthiques "d'eau claire".

On a remarqué deux tendances dans les relevés de polluants :

a) Les pesticides, mesurés en faibles concentrations dans les sédiments, étaient plus concentrés dans le tissu benthique au voisinage des sorties d'égouts pluviaux et des effluents d'usines de traitement des eaux usées. D'après d'autres études du ministère de l'Environnement, il semble que ces pesticides, libérés en faibles concentrations, soient absorbés par des organismes benthiques au voisinage des rejets. Au contact des sédiments essentiellement anaérobiques, les pesticides sont alors décomposés en un délai relativement court.

b) Le benthos tire le mercure, les PCB (polychlorobiphényles), le cuivre et le zinc des sédiments. L'absorption de ces paramètres dépend du contenu en matières organiques des sédiments, en particulier de leur teneur en composés extractibles solvants (huiles et graisses). Dans les régions à teneur élevée en matière organique, l'absorption était très faible, mais les concentrations de cuivre, de zinc, de mercure et de PCB étaient généralement des plus élevés dans les sédiments. Par contre, l'absorption la plus élevée se présentait dans les sédiments à faible teneur en matière organique.

Les concentrations de zinc et de cuivre dans les organismes ne se rattachaient pas au concentrations totales de ces métaux dans les sédiments, mais elles semblaient liées à des fractions géochimiques spécifiques. La phase F4 (fractions modérément réductibles associées aux particules porteuses de fer et de manganèse) était la source essentielle de zinc pour le biotope, alors que, pour le cuivre, c'était la phase F3 (organique/sulfure).

CONCLUSIONS

Les résultats de ces études font fortement croire que les sédiments contaminés sont une source de polluants pour les organismes benthiques; ils peuvent avoir des effets toxiques sur les organismes benthiques en éliminant totalement leur survie ou en réduisant leur éventail à quelques espèces tolérantes. La survie des organismes benthiques dans les sédiments pollués et la concentration de certains polluants dans les tissus de ces organismes soulèvent des inquiétudes quant au transfert possible de ces polluants aux organismes situés en aval dans la chaîne alimentaire.

Les effets de rejets continus, comme l'effluent des égouts pluviaux et des usines de traitement des eaux usées, ne peuvent être ignorés, car ils constituent la source principale d'inquiétude dans les régions à sédiments contaminés. Toute stratégie de gestion visant à améliorer la qualité des sédiments doit d'abord s'attaquer à l'apport de ces rejets.

1.0 INTRODUCTION

In 1983, the Ontario Ministry of the Environment carried out the first phase of the In-Place Pollutants Program. The studies associated with this phase of the program were designed to obtain information on the physical and chemical characteristics of surficial sediment and the levels of contaminants in representative species of benthic invertebrates in selected areas of the Great Lakes (Sub objectives 1 and 4 as outlined in Volume II of this report).

Specifically, the studies of Phase 1 were designed to address the following objectives:

1. To obtain up-to-date information on the physical and chemical characteristics of surficial sediment in selected areas of the Great Lakes. This information will be used:

    (a) to determine the variability in contaminant distribution within and among the various study locations.

    (b) to determine the influence of sediment grain size on contaminant levels.

2. To examine the partitioning of metals among various geochemical phases of the <63 μm sediment fraction which is the fraction normally ingested by benthic organisms. This information will be used:

    (a) to estimate the biological and physico-chemical availability of metals.

    (b) to determine which phase or combination of phases contributes to the levels found in indigenous benthic species.

3. To determine contaminant concentrations in selected benthic macroinvertebrates. This information will be used:

(a) to determine which contaminants bioconcentrate in organisms and the magnitude of uptake in relation to sediment levels.

The most direct influence of contaminants in sediments is expected to be exerted on the organisms that inhabit the sediment. Such influence can include the elimination of certain species as a result of the toxic effects of contaminants (to be discussed in a future report) or elevated levels of certain contaminants in the organisms that are able to survive. This latter aspect forms the major thrust of the Phase 1 studies.

In assessing the levels of contaminants in benthic organisms, consideration must be given to the spatial variability in distribution of contaminants in sediment (Volume II of this report) on both local and regional scales. This variability can be attributed to factors such as contaminant sources, sediment type and the hydrologic conditions that influence sediment movement and deposition. As a result, the number of stations within a given location and the study locations were selected to provide an adequate data base to address this issue.

Contaminant uptake by biota depends, to a large extent, on the form in which the contaminant exists in sediment. This is especially characteristic of the heavy metals, of which only a fraction of the total levels in sediment may be bioavailable.

A laboratory approach using selective chemical leaching in addition to total digestion (bulk chemistry) was used in the Phase 1 studies to determine how the metals partition among the various geochemical fractions of sediment. This procedure offers a considerable advantage over the standard bulk chemistry procedures by providing information on the source of metals (natural vs. anthropogenic), the chemical association of metals within sediment and the biological and physico-chemical (Eh/pH related) availability of metals.

This report describes the field and laboratory studies associated with the Phase 1 studies and discusses the findings. Because of the large data base and number of statistical analyses carried out, only pertinent information will be provided in this volume. Other information will be presented in Volume IV of this report series

2.0 METHODS

2.1 Field Sampling

During the 1983 field season, 87 stations were sampled from 12 locations in Lake Ontario and four of the Great Lakes Interconnecting channels. The locations and number of stations are given in Table 2.1.

2.1.1 Sediment

Sediment collection was carried out using a 23 cm x 23 cm, Ponar grab sampler. Sample jars were filled with the top 5 cm of sediment from the ponar. pH and Eh readings were taken for each sediment sample in the field with a Corning pH and Eh meter.

The sediment samples were kept at 4°C, returned to Toronto and submitted for bulk chemical analysis on the entire sediment matrix and sequential extraction analysis on the <63 μm fraction.

2.1.2 Benthic Invertebrates

Sediment collected by the Ponar grab sampler was sieved through a U.S. #30 mesh wash bucket. The sieved samples were stored in large plastic pails and transported to the laboratory where they were sorted into various taxonomic groups. The predominant organisms obtained were from the following groups: Lumbriculidae and Tubificidae.

Approximately 5-10 gms (wet weight) of tissue were required to carry out duplicate chemical analyses.

2.2 Laboratory Procedures

2.2.1 Bulk Sediment Chemistry

Sediment samples were submitted to the MOE Rexdale laboratory for bulk chemical analyses on the entire sediment matrix. The bulk chemical

TABLE 2.1 - **Study Locations and Number of Stations**
(See Figure 2.1 - 2.11 for Station Locations)

Study Locations	No. of Stations
Lake Ontario -	
Windermere Basin (in Hamilton Harbour)	5
Outside Hamilton Harbour	5
Humber Bay	16
Toronto Harbour	10
Ashbridges Bay	2
East Headland	5
Toronto Eastern Waterfront (Beaches, Bluffs)	9
Frenchman Bay	5
Interconnecting Channels* -	
St. Clair River	8
St. Marys River	8
Niagara River	9
St. Lawrence River (near Wolfe Island)	5

* The Detroit River was not included in the Phase 1 studies.

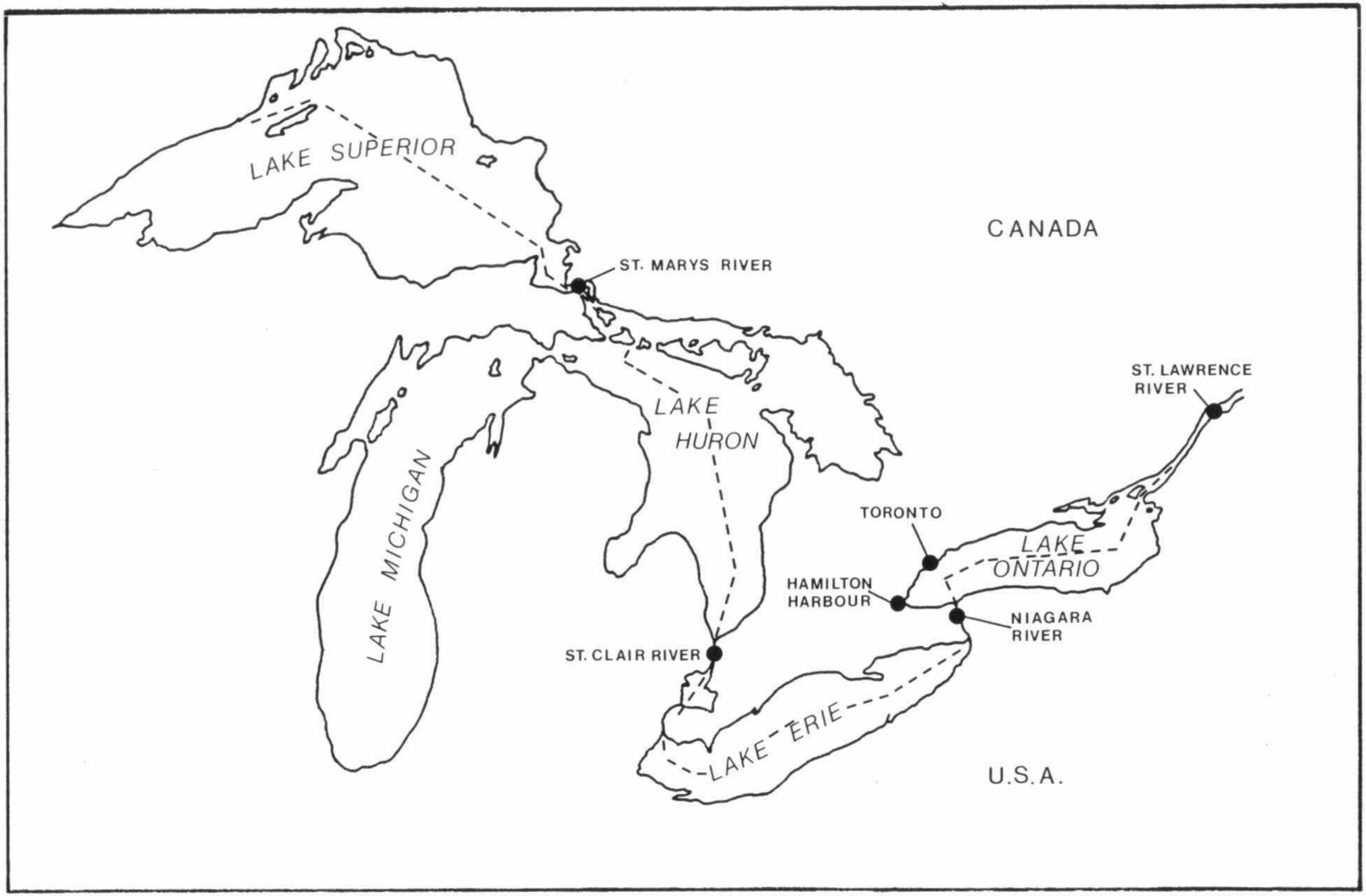


FIGURE 2.1 : PHASE 1 STUDY AREAS

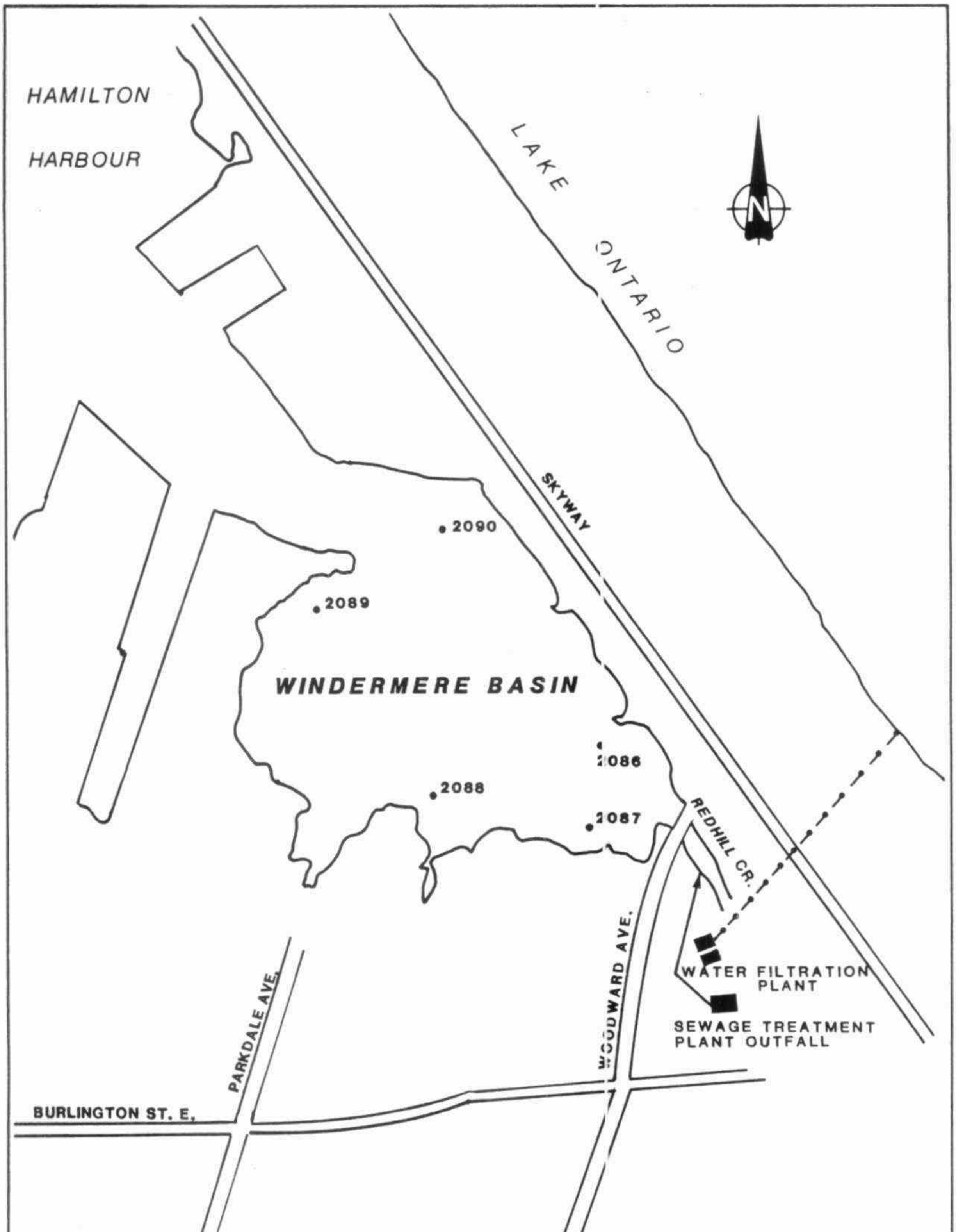


FIGURE 2.2 : STATION LOCATIONS– WINDERMERE BASIN

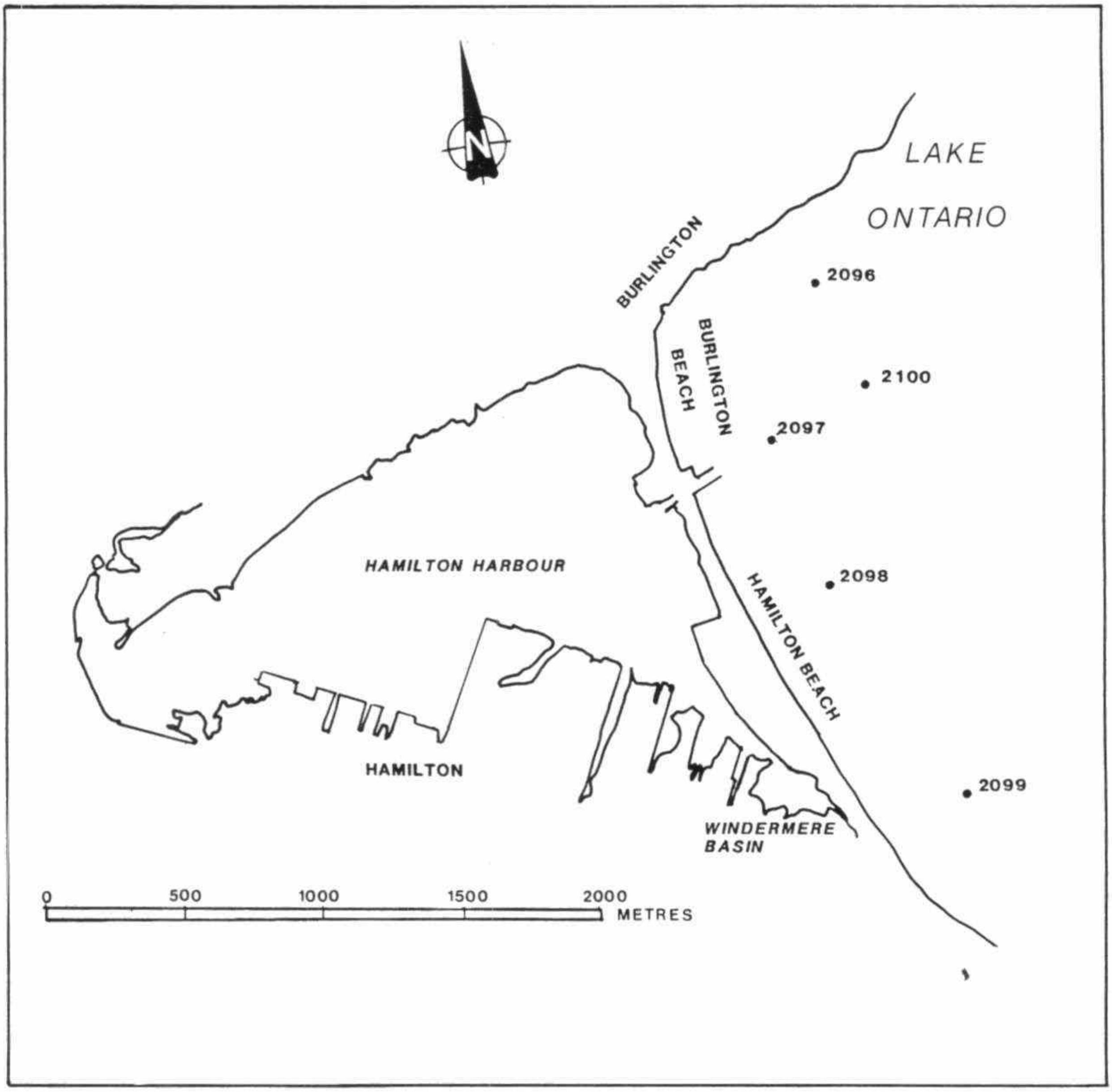


FIGURE 2.3: STATION LOCATIONS- OUTSIDE HAMILTON HARBOUR

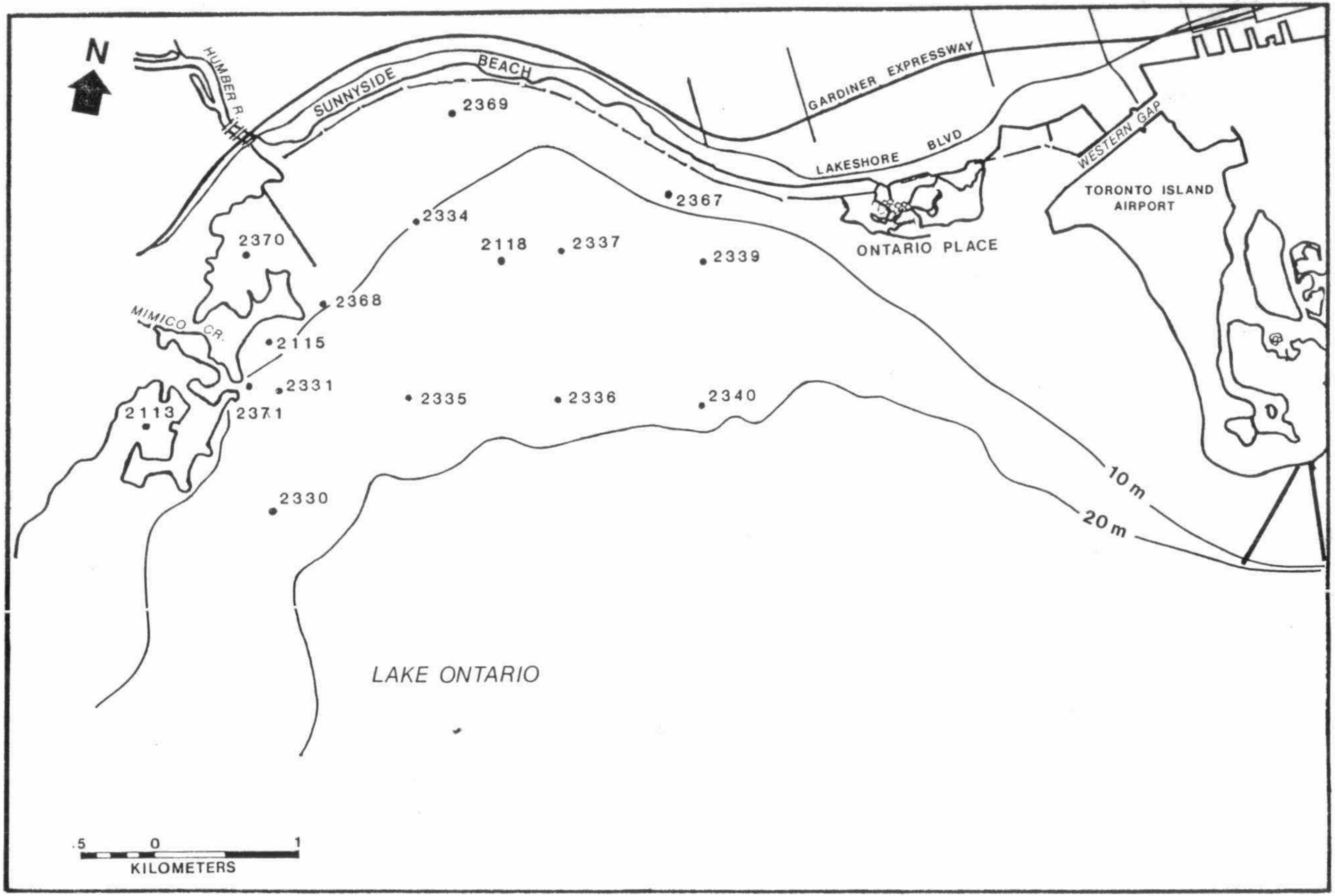


FIGURE 2.4: STATION LOCATIONS- HUMBER BAY

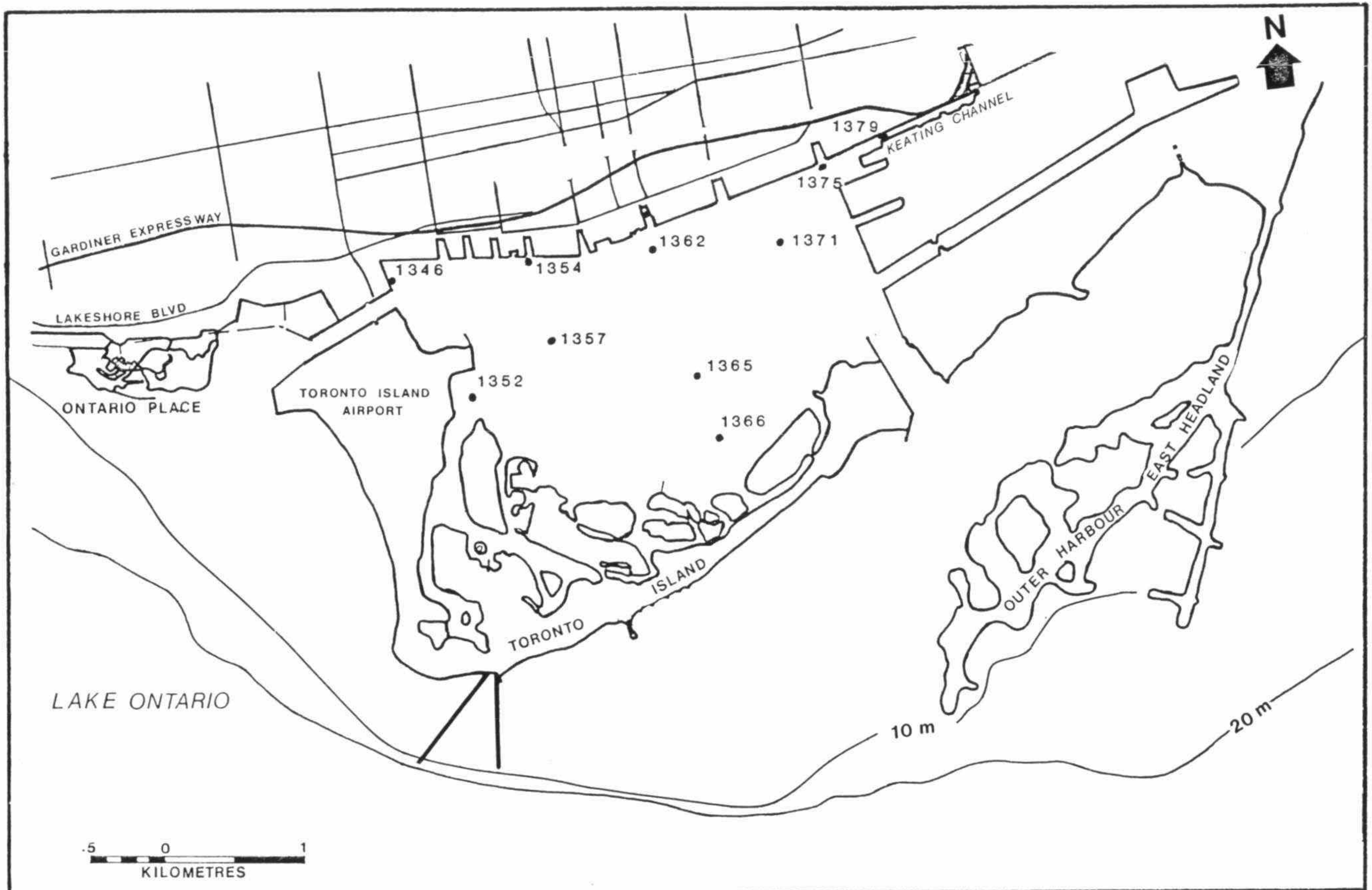


FIGURE 2.5 : STATION LOCATIONS– TORONTO HARBOUR

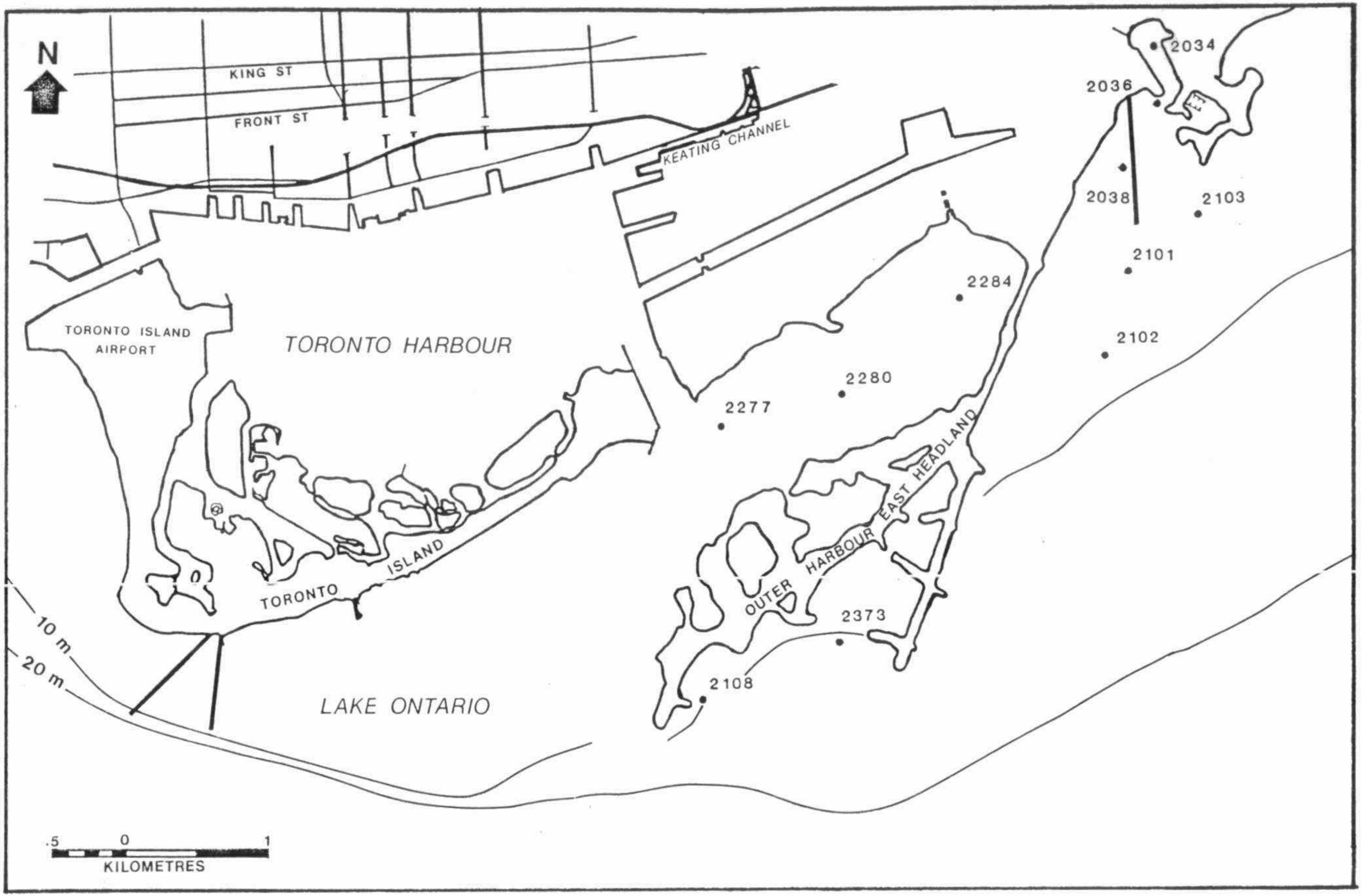


FIGURE 2.6 : STATION LOCATIONS- EASTERN HEADLAND AND ASHBRIDGES BAY

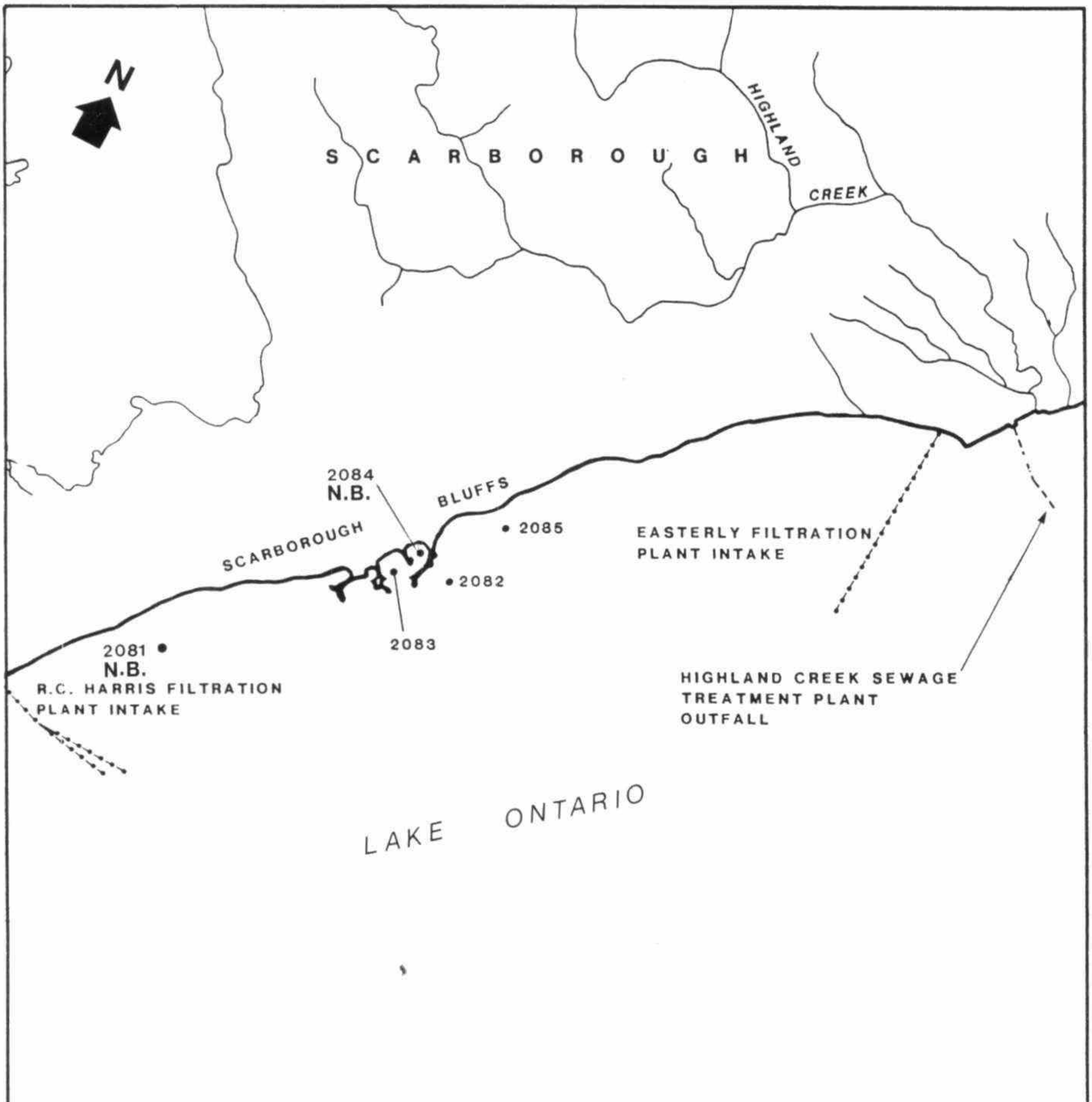


FIGURE 2.7 : STATION LOCATIONS- SCARBOROUGH BLUFFS

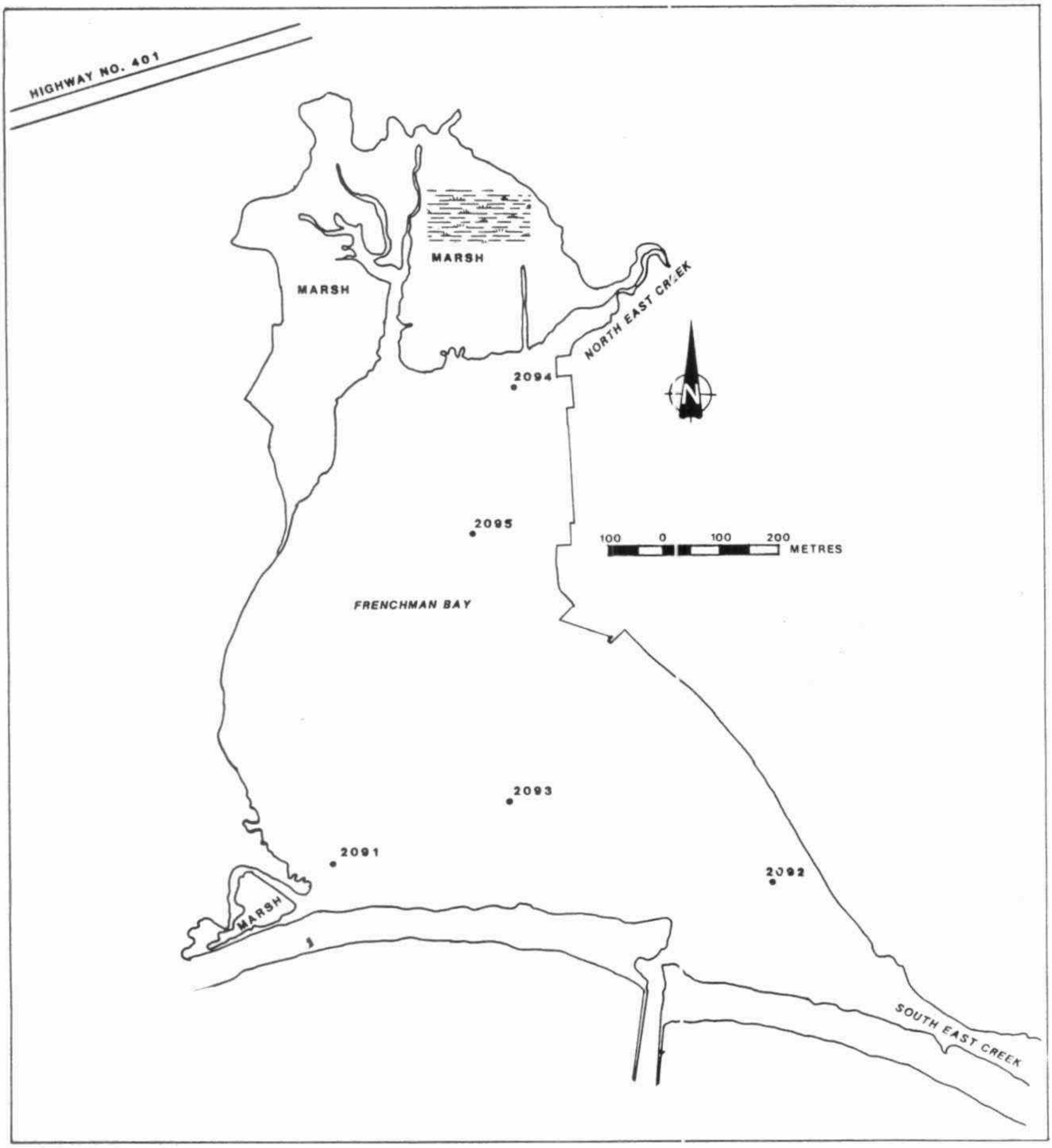


FIGURE 2.8 : STATION LOCATIONS- FRENCHMAN BAY

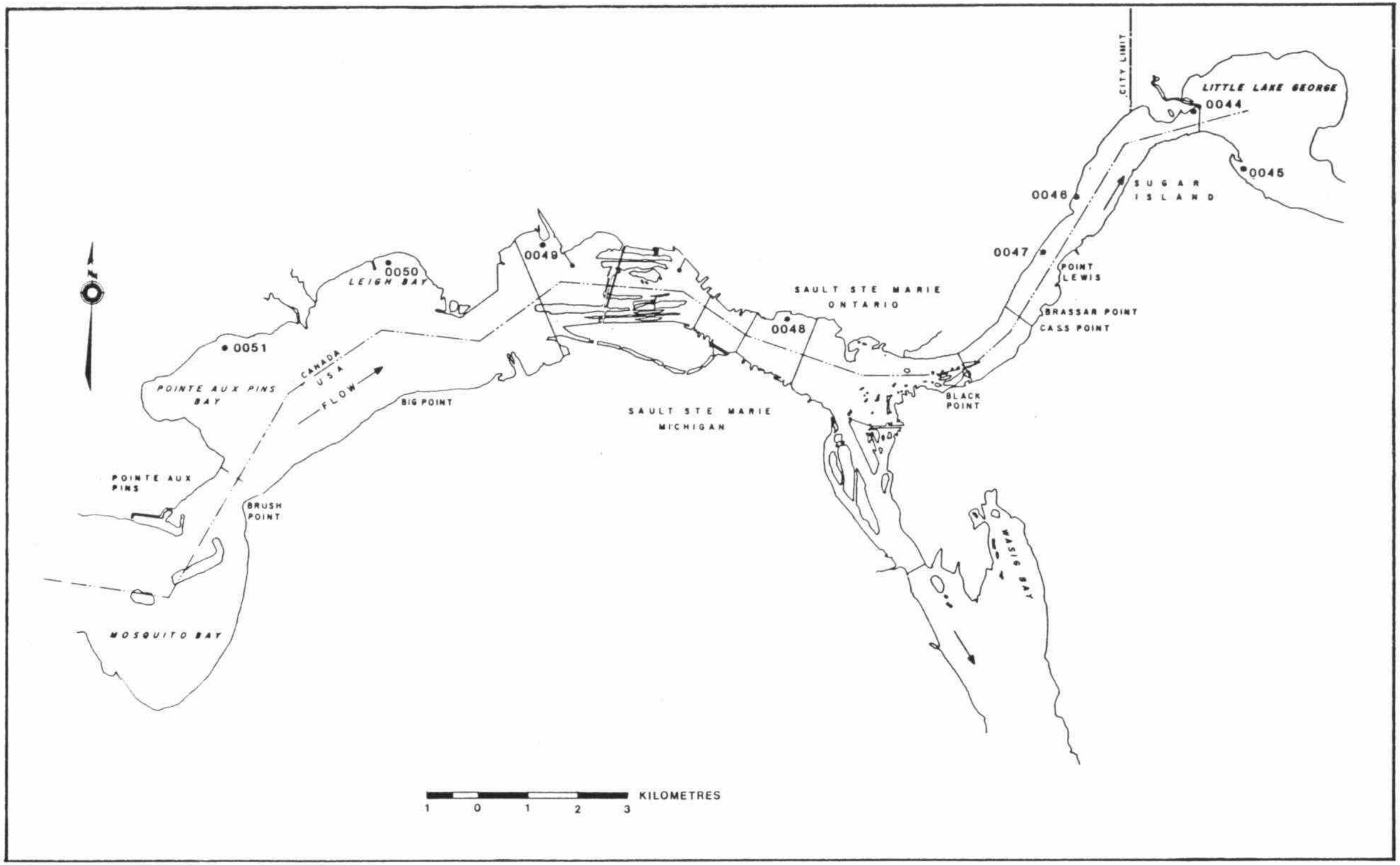


FIGURE 2.9 : STATION LOCATIONS– ST. MARYS RIVER

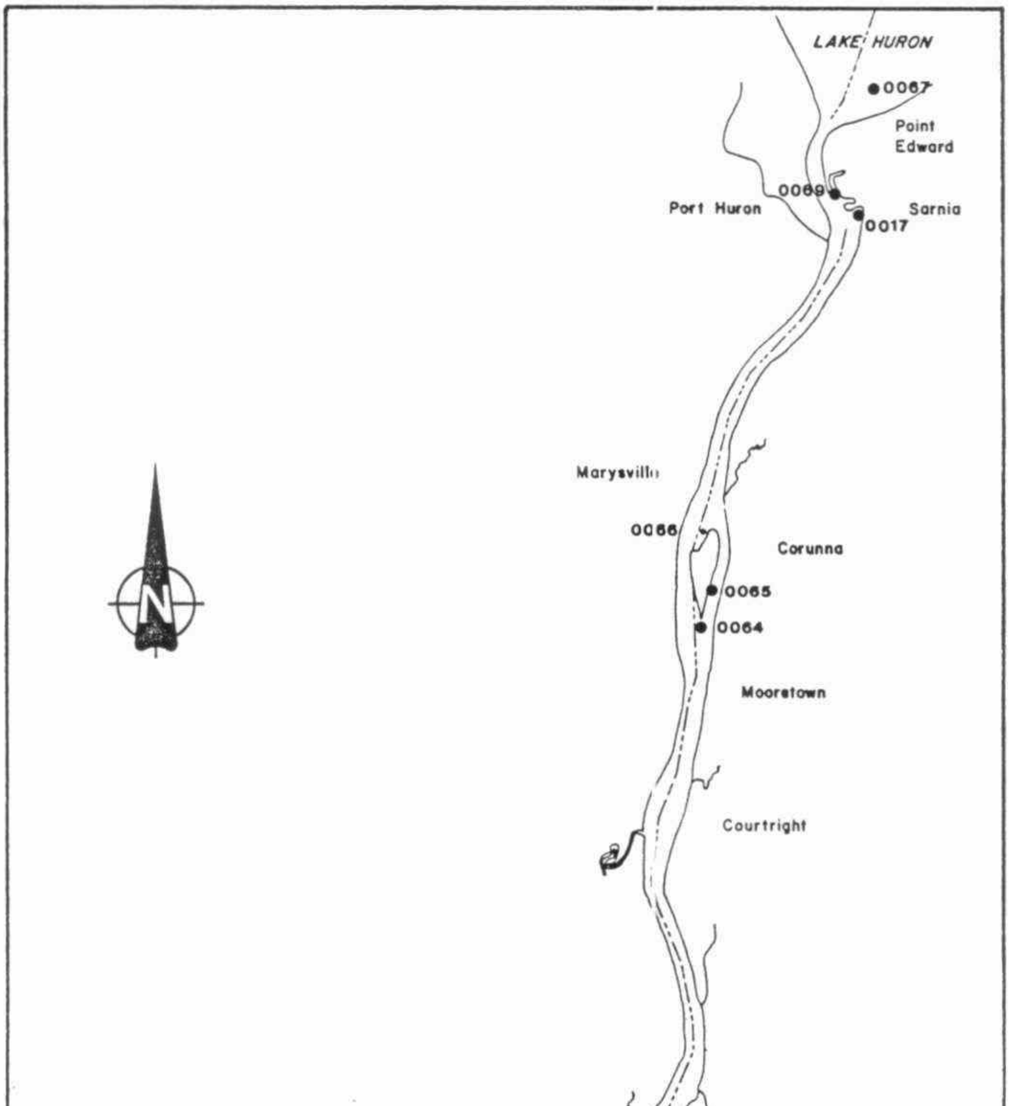


FIGURE 2.10 : STATION LOCATIONS - ST. CLAIR RIVER

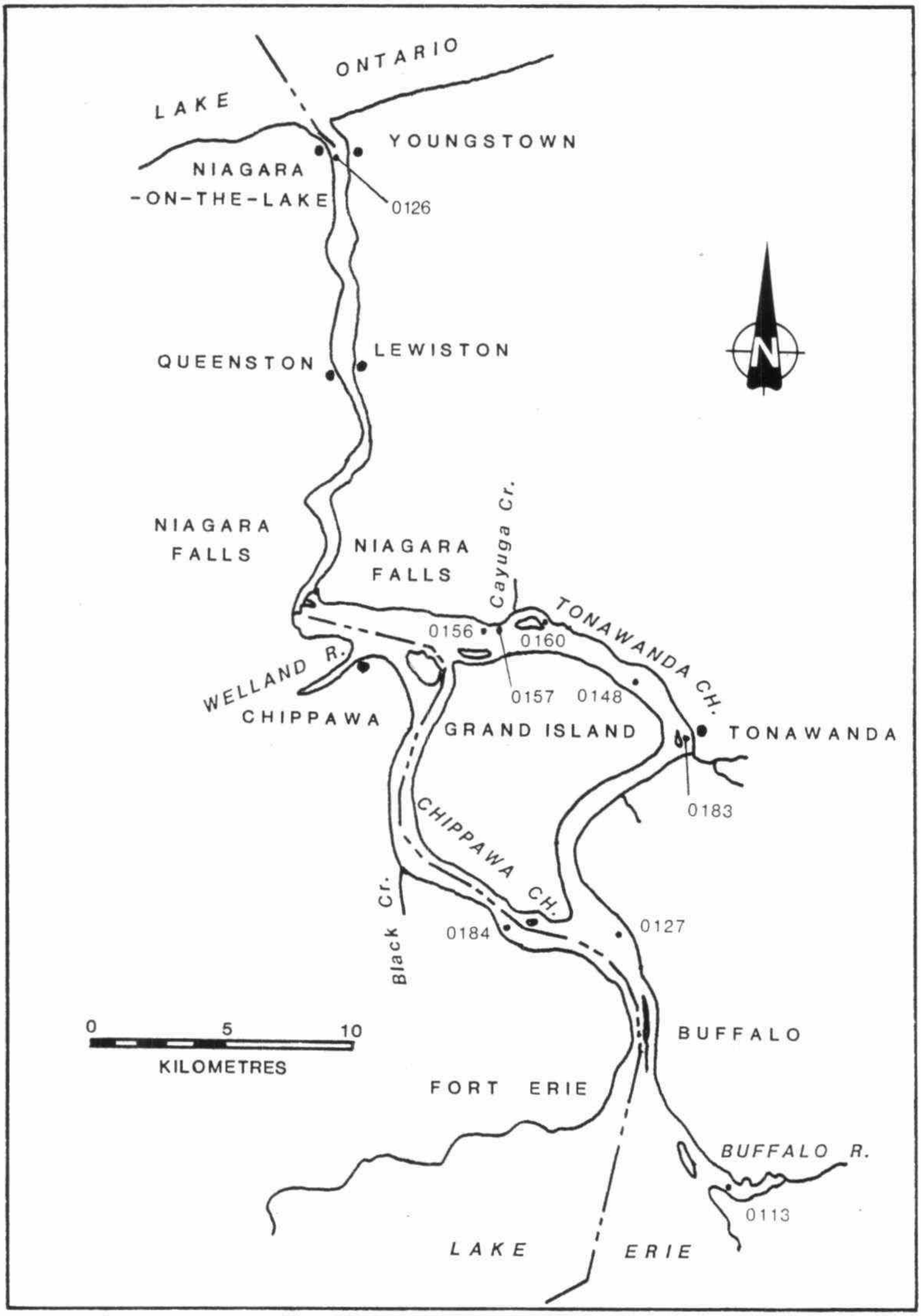


FIGURE 2.11: STATION LOCATIONS- NIAGARA RIVER

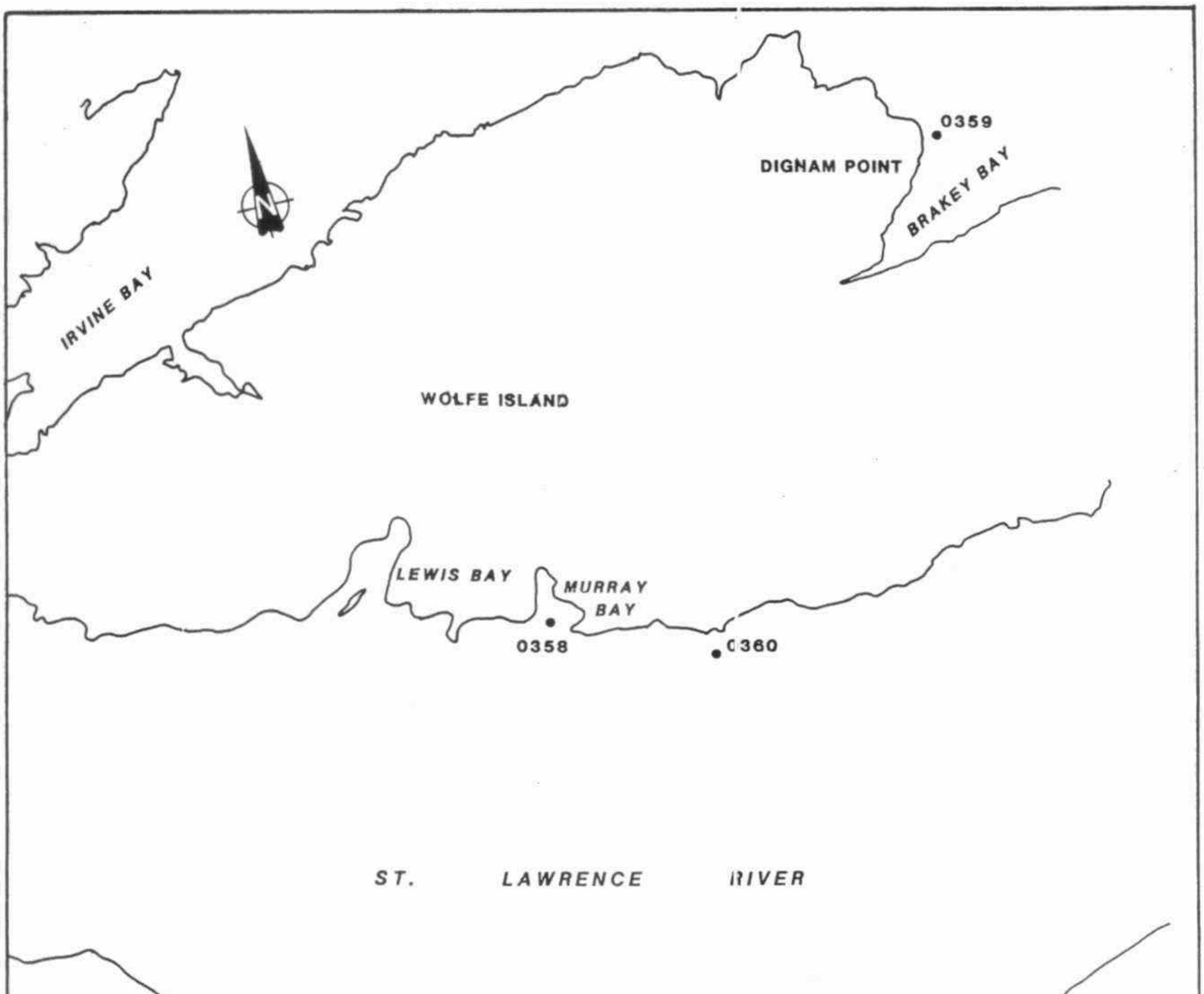


FIGURE 2.12 : STATION LOCATIONS- ST. LAWRENCE RIVER

analyses included loss on ignition, total Kjeldahl nitrogen, total organic carbon, total phosphorus, chromium, iron, manganese, mercury, cadmium, zinc, copper, lead, arsenic, solvent extractables (oil and grease), PCBs, pesticides and grain size.

Analyses were carried out in accordance with the MOE procedures (Ontario Ministry of the Environment, 1983) and all parameters were reported on a dry weight basis. Detection limits for the various analytical procedures are outlined in Volume IV of this report.

2.2.2 Metal Analysis In < 63 μm Fraction Of Sediment

Sequential Extraction

The <63 μm fraction includes sediment material such as very fine sand, silt and clay. This fraction consists of the size range of sediment that is normally ingested by benthic macroinvertebrates (Krantzberg and Bailey, 1983). This fraction was subjected to a sequential chemical leaching procedure to determine the geochemical partitioning of the metals.

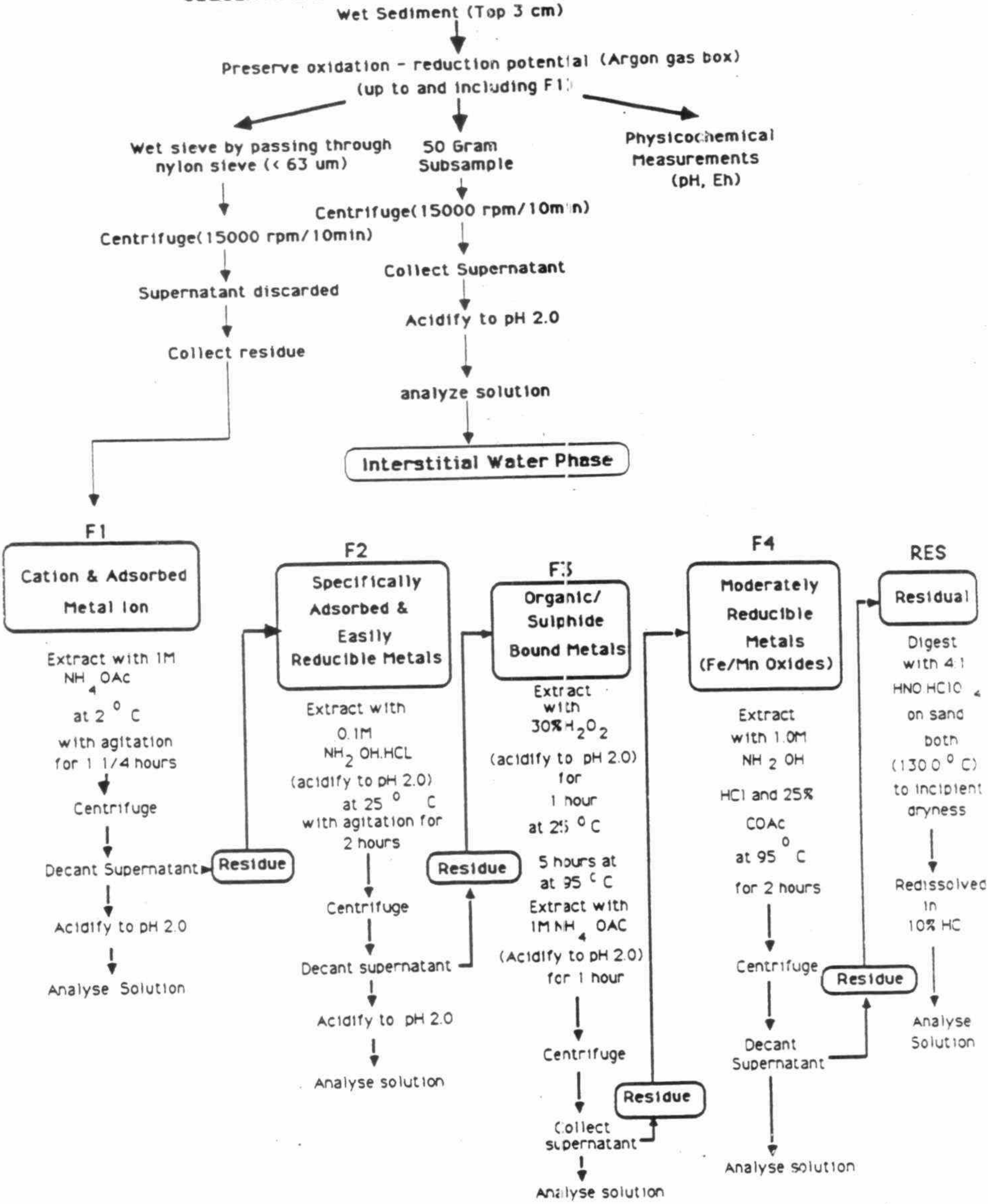
The sequential extraction procedure (see Volume II of this report and Fig. 2.13) was applied to seven metals: cadmium, copper, zinc, lead, arsenic, iron and manganese. The geochemical phases identified in the procedure were:

- IW - pore water
- F1 - cation exchangeable/weakly adsorbed metal ion
- F2 - specifically adsorbed and easily reducible metals
- F3 - organic/sulphide bound metals
- F4 - moderately reducible (Fe/Mn oxides) metals
- F5 - residual metal

2.2.3 Benthic Invertebrates

The benthic samples obtained in the field, were hand-picked and cleaned under running water in the laboratory. The organisms were blotted dry and then subsampled into three portions for the following:

FIGURE 2.13
SEQUENTIAL EXTRACTION OF SEDIMENT - Bound Metals



- identification - 50 oligochaetes in 5% formaldehyde
  - 10-20 individuals of other organisms in 5% formaldehyde
- metal analysis - the organisms were wrapped in plastic film and frozen
- PCB/pesticides scan - the organisms were wrapped in aluminum foil and frozen.

Metal Analysis

Analyses were carried out for cadmium, copper, iron, lead, manganese, zinc, mercury and arsenic on the benthic samples . Mercury analysis consisted of digesting the organisms in a sulphuric acid - potassium permanganate solution and determinations of mercury concentrations were made by automated stannous chloride reduction and cold vapour AAS (atomic absorption spectrophotometry). The other metals were analysed by digesting the organisms in nitric acid-perchloric acid solution and chemical determinations were made by flame AAS.

PCB/Pesticide Analysis

The frozen samples were homogenized and digested for 12 hours in concentrated hydrochloric acid at 25°C. The digest was then extracted with a methylene chloride/hexane mixture. The extract was neutralized with sodium bicarbonate, dried by filtering through anhydrous sodium sulphate and evaporated.

The residue was placed in a clean-up column with 5 g of 100/200 mesh Florisil. The column was eluted successively with hexane, 25% methylene chloride/hexane and methylene chloride to obtain values for the PCBs and organochlorine pesticides. The compounds determined in each of the three fractions are shown below.

I - Hexane fraction: PCBs, HCB, Heptachlor, Aldrin, p,p'-DDE, Mirex

II - 25% Methylene chloride/ hexane fraction:

alpha-chlordane
gamma-chlordane
o,p'-DDT, p,p'-DDD, p,p'-DDT

III- Methylene chloride fraction: Heptachlor epoxide, alpha-endosulfan, beta-endosulfan, dieldrin, endrin.

All fractions were evaporated to near dryness and made up to 1 ml in iso-octane. Each fraction was analyzed by a "Varian Vista 6000" gas chromatograph interfaced to a "Vista 402" chromatography data system.

2.2.4 Dry Weight Conversion of Contaminant Levels in Benthic Tissue

Contaminant levels in the benthic organisms were determined on a wet weight basis and the values obtained were converted to dry weight using the following relationship based on information from Howmiller (1972).

$$\text{Dry Weight Contaminant Value} = \text{Wet weight Contaminant Value} \times \frac{100}{15.9}$$

[where the dry weight of tissue was 15.9% of the wet weight.]

2.2.5 Correction for Gut Content

Correction for contaminants in the sediment remaining in the gut of the organism at the time of analysis was made by ashing the organisms at 500°C and determining the weight of the remaining residue.

The concentration of contaminants in the residue was calculated as follows:

$$C\ corr\ tiss = \frac{C\ org - (C\ sed \times K\ ash)}{(1 - K\ ash)}$$

where C corr tiss = contaminant concentration in the benthic tissue corrected for gut content

C org = contaminant concentration (dry weight) in the organism (tissue and gut)

C sed = contaminant concentration in the < 63 μm sediment (bulk analysis of <63μm fraction)

K ash = residue remaining after ashing the organism at 500°C as a percentage of the bulk chemical value. i.e. $K\ ash = \frac{\%\ ash}{100}$

2.3 Statistical Assessment of Data

Data on metal levels in organisms and sediment are not usually normally distributed. As a result, all metal data were log-transformed to provide a normal distribution. (Shuman *et al*. 1977).

A statistical software package "Microstat" (developed by Ecosoft) was used to carry out the statistical analyses.

The concentrations of several variables (mainly pesticides) were generally below the analytical detection limits. In these cases, a value of 1/2 of the detection limit was substituted in the data set. Distribution characteristics of trace organics data were complicated by the presence of results less than the detection level. In these cases a value of one half the detection level was used in order to compute a reasonable estimate of the mean. Although these estimates are biased, the uncertainty associated with this procedure was assumed to be relatively negligible in comparison with the large degree of variability present in the data (i.e. standard deviations are not substantially altered by this procedure). Duplicate analyses of contaminants in benthic organisms were reported as mean values.

3.0 RESULTS

3.1 Sediment Bulk Chemistry

Results from bulk chemical analysis on the total sediment matrix are provided in Tables in Volume IV of this report and summary statistics are provided in Table 3.1. Plots showing the distribution of parameters among the stations are presented in Figure 3.1. Table 3.2 shows the study locations corresponding to the station numbers in Figure 3.1. Because pesticides were detected at very low levels in sediment and the small number of stations from which pesticide data were obtained, these compounds will not be discussed in this section but will be addressed in the section outlining the biological data.

3.1.1 General Parameter Distribution

The pH readings obtained were generally close to neutral (pH 7.0) except for two stations outside Hamilton Harbour and one station in St. Marys River, where values of less than pH 6 were detected. The reasons for these low readings were not readily apparent.

Redox potential (Eh) ranged from -520 mv to +430 mv, with the sediment from most stations showing negative values. This indicates that most of the sediments sampled were anaerobic (i.e., reducing conditions).

Loss on ignition, which is a measure of the organic content of sediment, ranged from 0.1% to 29.0% with most stations showing values of less than 10%. The highest values noted were in Windermere Basin and Frenchman Bay.

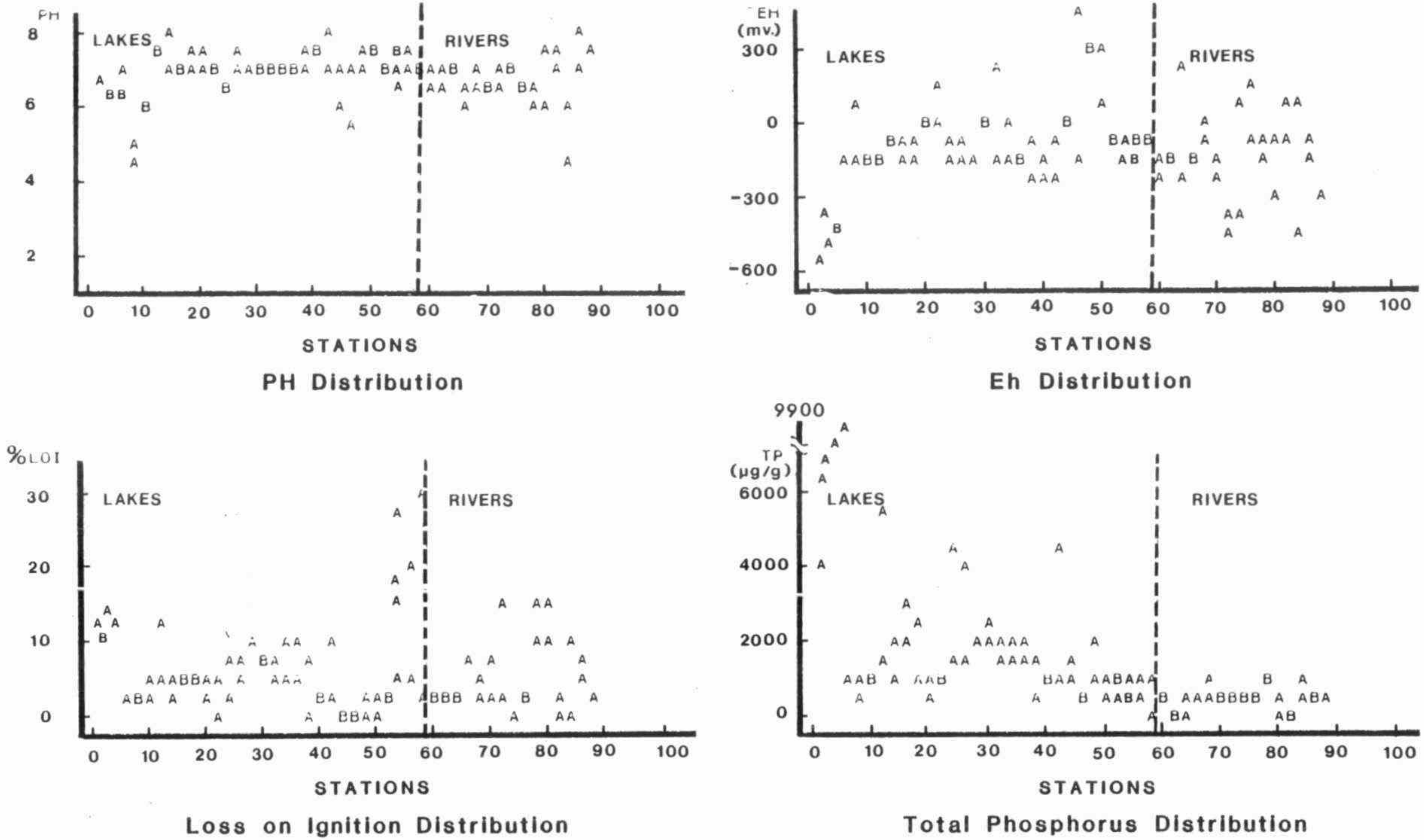
The variability in total phosphorus concentrations was much greater among the lake stations compared to the river stations. Although the range in variation among stations sampled was between 100 ppm and 9900 ppm; most of the values were below 2000 ppm. High values of total phosphorus were noted in Windermere Basin.

Table 3.1: Sediment Bulk Chemistry Summary Statistics

[all values in ppm(dry wt.) except pH, Eh(mv), and LOI(%)]

Parameter	N*	Mean	Std. Dev.	Median	Minimum	Maximum
Eh	87	-103	183	-155	-520	430
TP	86	1275	1648	900	100	9900
TKN	86	1862	1498	1100	100	6100
TOC	49	21395	20809	16000	10	82000
Cu	86	58.8	75.5	38	2	430
Cr	86	74.9	128	44	7.6	900
Cd	86	2.82	3.45	0.73	0.2	18
Fe	86	19204	8421	20000	4700	80000
Pb	86	108	154	56	3	570
Zn	86	218	351	110	10	2800
Mn	84	390	173	390	88	1500
SOL	84	4433	5500	2150	180	24410
PCB	81	0.19	0.3	0.03	0.02	3.1
LOI	86	5.67	4.81	4.6	0.1	29
Hg	86	0.23	0.26	0.11	0.01	2.2
As	74	5.21	3.4	4.29	0.57	16.1
pH	87	6.79	0.63	6.8	4.25	7.94

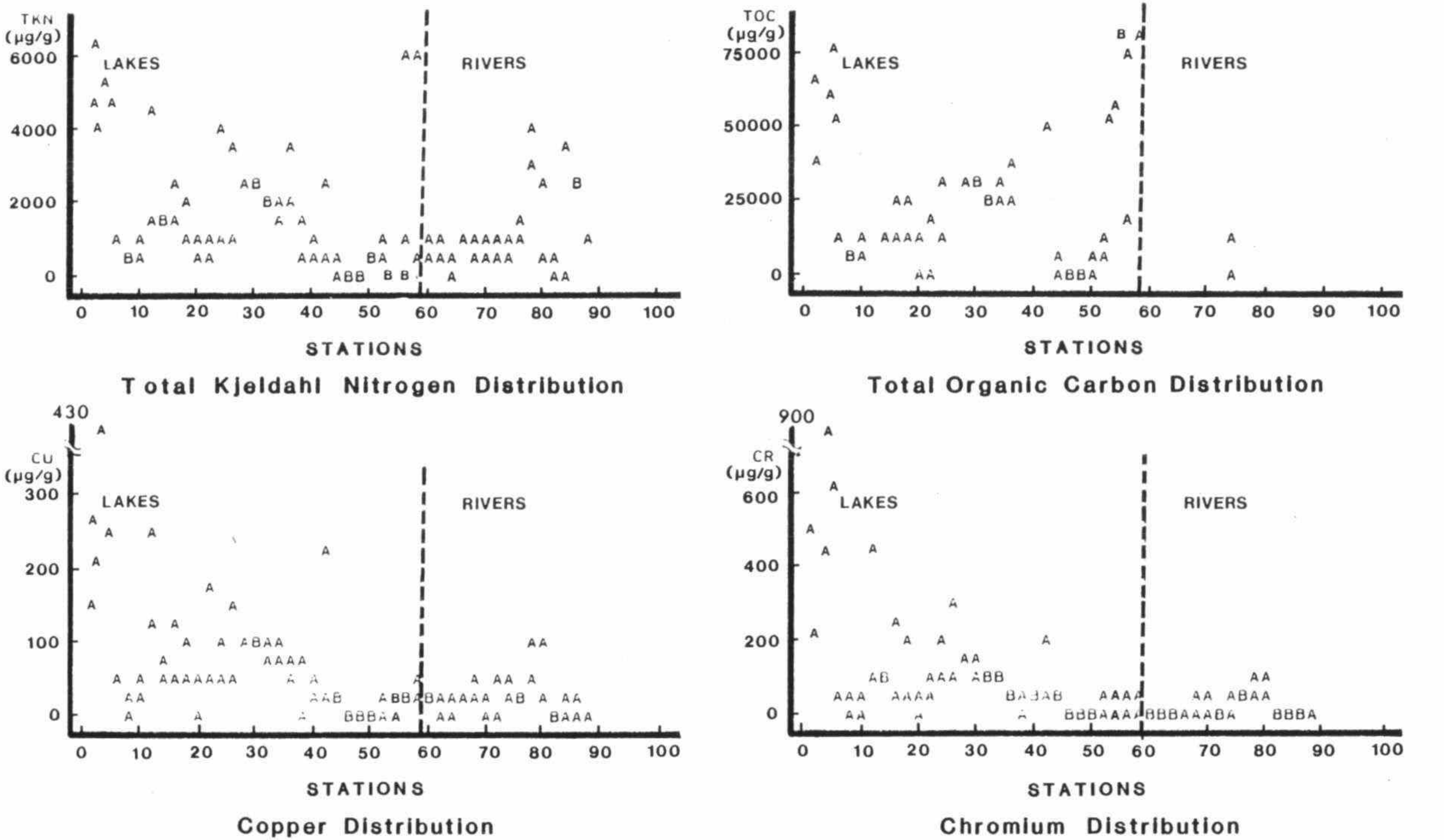
* N - Refers To The Number Of Stations



LEGEND: A = 1 OBS, B=2 OBS, ETC

For study locations corresponding to station numbers refer to Table 3.2

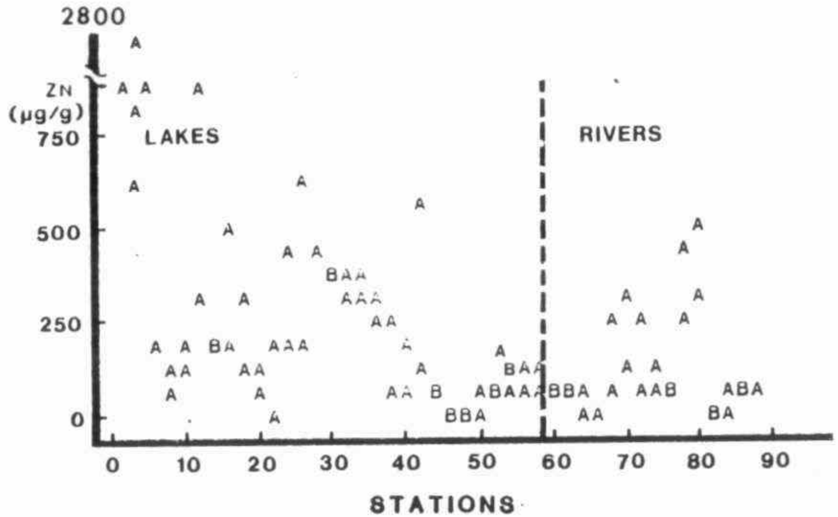
FIGURE 3.1: DISTRIBUTION OF CHEMICAL PARAMETERS IN SEDIMENT



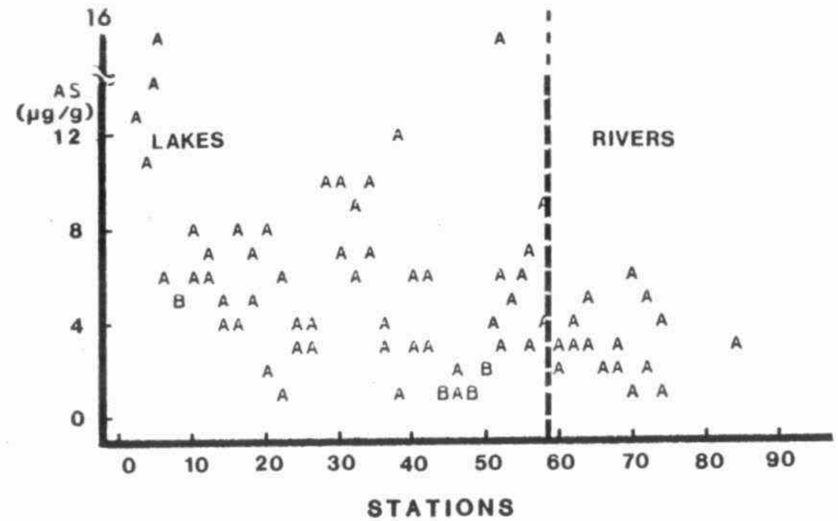
LEGEND: A=1 OBS, B=2 OBS, ETC.

For study locations corresponding to station numbers refer to Table 3.2

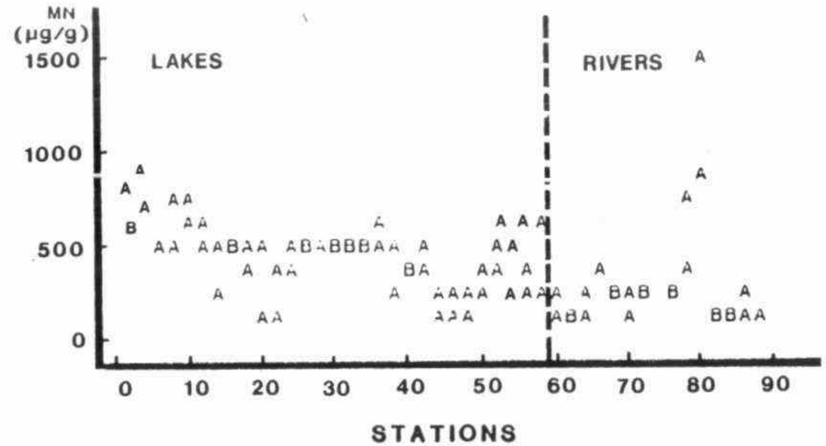
FIGURE 3.1 : DISTRIBUTION OF CHEMICAL PARAMETERS IN SEDIMENT cont'd



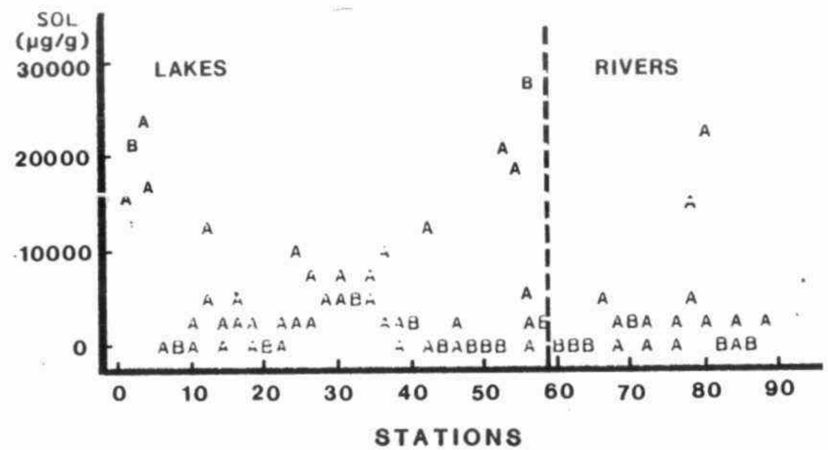
Zinc Distribution



Arsenic Distribution



Manganese Distribution

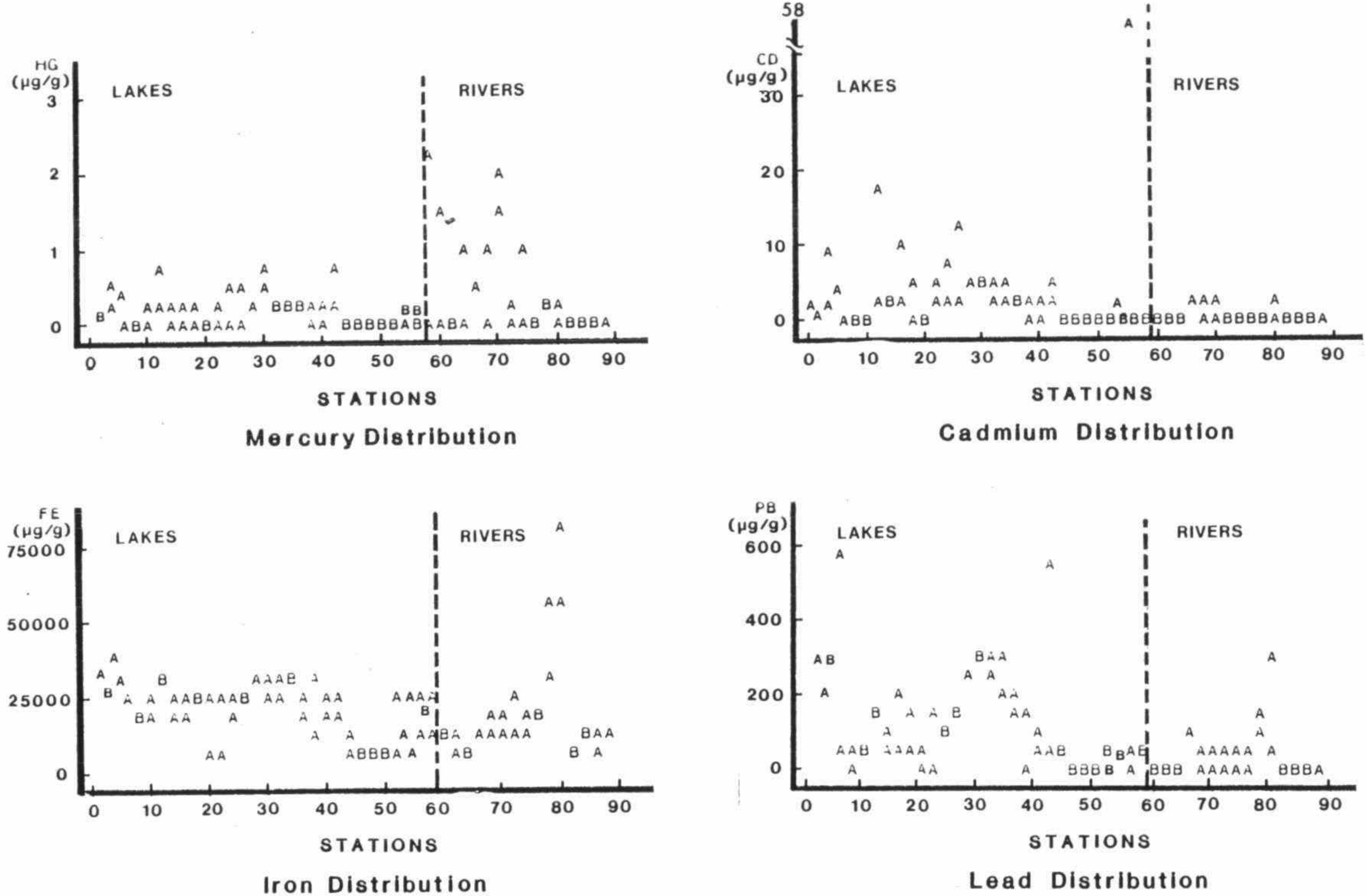


Solvent Extractables (oil and grease) Distribution

LEGEND: A=1 OBS, B=2 OBS, ETC.

For study locations corresponding to station numbers refer to Table 3.2

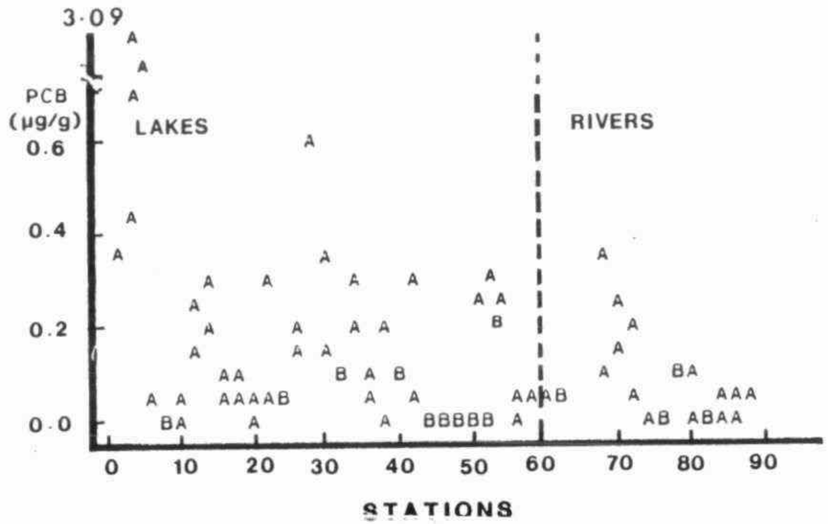
FIGURE 3.1 : DISTRIBUTION OF CHEMICAL PARAMETERS IN SEDIMENT cont'd



LEGEND: A=1 OBS, B=2 OBS, ETC.

For study locations corresponding to station numbers refer to Table 3.2

FIGURE 3.1 : DISTRIBUTION OF CHEMICAL PARAMETERS IN SEDIMENT cont'd



PCB Distribution

LEGEND: A=1 OBS, B 2=OBS, ETC.

For study locations corresponding to station numbers refer to Table 3.2

FIGURE 3.1 : DISTRIBUTION OF CHEMICAL PARAMETERS IN SEDIMENT cont'd

TABLE 3.2: STUDY LOCATIONS CORRESPONDING TO STATION NUMBERS IN FIG. 3.1

Station Numbers	Study Locations	
1 - 5	Windermere Basin (in Hamilton Harbour)	
6 - 10	Outside Hamilton Harbour	
11 - 26	Humber Bay	
27 - 36	Toronto Harbour	
37 - 41	Eastern Headland	
42 - 43	Ashbridges Bay	
44 - 47	East side of the Headland	) Eastern
48 - 50	Scarborough Bluffs	) Toronto
51 - 52	Bluffers Park	) Waterfront
53 - 57	Frenchman Bay	
58 - 65	St. Clair River	
66 - 74	Niagara River	
75 - 82	St. Marys River	
83 - 87	St. Lawrence River	

Total Kjeldahl nitrogen, which like LOI, is a measure of the organic content of sediment, ranged from 100 ppm to 6100 ppm. High values were noted in Windermere Basin and Frenchman Bay.

Total organic carbon showed the widest range in concentration (10 ppm to 82,000 ppm). Most values were below 25,000 ppm with the highest levels in Windermere Basin and Frenchman Bay.

Copper, chromium and cadmium concentrations showed greater variability among the lake stations while mercury concentrations varied considerably among the river stations.

Iron, manganese and solvent extractables (oils and greases) showed considerable variations among the stations in the St. Marys River. The highest values for these parameters were noted in the St. Marys River and Windermere Basin.

Elevated levels of PCBs were found in Windermere Basin, Toronto Harbour, Humber Bay and at the Toronto East Headland in order of decreasing concentrations.

3.1.2 Contaminant Variability Among Study Locations

Based on the apparent regional differences in contaminant levels in sediment (Figure 3.1), a comparative evaluation of mean concentrations of chemical parameters obtained from the bulk chemistry analyses was carried out. The values for the various parameters are provided in Tables 3.3 and 3.4 for the Lake Ontario and the interconnecting channel locations respectively.

Among the lake stations, Windermere Basin sediment showed excessively high values for all parameters measured (except mercury which was higher in Toronto Harbour), followed by Toronto Harbour and Humber Bay. The levels of contaminants in Windermere Basin, Toronto Harbour and Humber Bay greatly exceeded the mean contaminant concentrations of Lake Ontario sediments for most parameters. Mean contaminant concentrations of Lake

Table 3.3 Mean Concentrations of Chemical Parameters In Sediment from Lake Ontario Locations

[all values in ppm dry wt. except LOI(%)]

Parameter	Windermere Basin (Hamilton Harbour)	Outside Hamilton Harbour	Humber Bay	Toronto Harbour	Toronto East Headland	Eastern Toronto Waterfront	Frenchman Bay	Lake Ontario Surficial Sediment **
Pb	348	38	104	271	83	17	54	107
Zn	1470	127	280	339	129	35	105	214
Cu	266	28	90	90	38	9	31	50
Fe	33800	20600	22169	26700	21520	13150	19200	55700
Mn	728	650	417	493	358	296	500	3200
Cr	538	31	133	92	46	19	32	48
TKN	5000	680	1780	2100	900	400	4520	ND
TP	6960	820	2100	1810	900	1040	880	2200
TOC	58000	8100	15100	29200	ND	4920	56000	ND
Sol. Ext.	20492	846	3605	5689	1926	602	1968	ND
Hg	0.35	0.07	0.22	0.47	0.17	0.02	0.05	0.65
Cd	5.24	0.46	5.00	3.93	1.54	0.36	12.27	2.50
As	13.60	5.90	4.70	6.90	5.00	0.40	8.60	3.30
LOI	14.40	2.78	4.98	7.26	3.22	1.59	17.54	1.96
PCBS	1.15	0.03	0.13	0.32	0.13	0.02	0.03	0.06

** = Whole lake mean values from R.L. Thomas and A. Mudroch (1979).

ND = No Data

Table 3.4 Mean Concentrations of Chemical Parameters in Sediment from the Great Lakes Interconnecting Channels Locations

[all values in ppm dry wt.]

Parameter	St. Lawrence River *	St. Clair River*	Niagara River *	St. Marys River *	Detroit River **
Pb	12.00	29.00	31.00	79.00	39.00
Hg	0.05	0.75	0.72	0.19	0.19
Zn	41.00	43.00	156.00	212.00	97.00
Cd	0.21	0.53	0.87	0.81	ND
Cu	12.00	15.00	29.00	37.00	22.00
Fe	11300.00	9237.00	14900.00	35087.00	14326.00
Mn	150.00	217.00	235.00	513.00	ND
Cr	17.00	13.00	24.00	40.00	24.00
TKN	1920.00	580.00	740.00	1630.00	ND
TP	640.00	250.00	640.00	530.00	ND
PCBS	0.03	0.03	0.14	0.04	0.07
Sol. Ext.	1414.00	1546.00	2000.00	6146.00	ND

* Data from Current Study (1983)

** Data from MOE 1980 Study(pers. comm. P. Kauss)

ND = No Data

Ontario sediments were obtained from Thomas and Mudroch (1979) (Table 3.3). The values represent mean concentrations for the whole lake surficial sediments (ie. depositional and nondepositional areas in Lake Ontario).

Notable exceptions were mercury, iron and manganese in Windermere Basin, Toronto Harbour and Humber Bay, total phosphorus in Toronto Harbour and Humber Bay and lead in Humber Bay.

The sediment from Frenchman Bay and Windermere Basin showed high organic enrichment based on values for LOI, TKN and TOC. For Frenchman Bay this enrichment is most likely a reflection of the peat-like substrate observed in the Bay during sampling. The relatively low levels of the other parameters in proportion to the organic content suggest that the organic enrichment of the bay is not significantly influenced by industrial/municipal discharges. An extremely high value for cadmium was obtained at one station, however this value cannot be confirmed without additional sampling. The high organic enrichment in Windermere Basin appears to be due mainly to the high levels of solvent extractables.

The sediments of Eastern Toronto Waterfront were relatively clean. This area is influenced by waves and currents which effectively minimize the deposition of fine-grained material such as silts and clays, with which any contaminant build-up would be associated.

The levels of contaminants in sediment from stations around the Toronto East Headland were considerably higher than the levels in Eastern Toronto Waterfront stations and also showed levels above those in the stations outside Hamilton Harbour (except Mn and As). The elevated levels of parameters around the East Headland relative to the Eastern Toronto Waterfront may be due to the localized deposition of material arising from the lake-filling activity at the headland.

Higher levels of mercury were noted in the St. Clair and Niagara Rivers compared to the other two interconnecting channels studied. As shown in Table 3.4, the St. Marys River had high levels of Pb, Zn, Cu, Mn, Fe, Cr

and solvent extractables compared to the other interconnecting channels. PCBs were also elevated in the Niagara River relative to other rivers (Table 3.4).

With the exception of metals and solvent extractables in the St. Marys River and mercury in the St. Clair and Niagara Rivers, the sediments of the interconnecting channels were of better quality compared to the lake stations, approximating those of the Eastern Toronto Waterfront.

In order to determine whether the differences in parameter concentrations between the rivers and lake stations were statistically significant, a normal test statistic (Z) was used to compare the means. The results are summarized in Table 3.5. There were no significant differences in the mean concentrations of Zn, Hg, Fe, TKN, Solvent extractables and PCBs between the lake and river stations. However, TP, Cu, Cr, Cd, Pb, Zn and As were significantly different, with much higher levels in the lake stations.

3.1.3 Inter-relationships Among Sediment Parameters

Parameters with similar distribution patterns in sediment usually show strong association when correlation coefficients between pairs of parameters are calculated. Very high positive correlations between parameters usually result when contaminants discharged from the same source are associated with the same "carrier particles" that behave similarly in the aquatic environment.

Correlation coefficients between various pairs of sediment parameters (chemical and grain size) are shown in Tables 3.6 and 3.7 for the lake and river stations respectively. The significance of the various relationships among the chemical parameters are summarized in Table 3.8.

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*"Carrier Particles" - refers to particulate matter to which contaminants are adsorbed. [The important *"carrier particles" with which contaminants are associated include organic material (measured as LOI, TOC or TKN), the hydrous oxides of Fe and Mn (mainly for metals) and clay minerals.]

TABLE 3.5: SUMMARY OF LAKE - RIVER COMPARISON

PARAMETER	Z	SIG-LEVEL	COMMENT
TP	6.40	≤.01	Significant
TKN	1.40	.16	Not Significant
CU	4.09	≤.01	Significant
CR	4.35	≤.01	Significant
HG	-1.73	.08	Not Significant
CD	4.66	≤.01	Significant
FE	0.49	.62	Not Significant
PB	3.79	≤.01	Significant
ZN	2.45	≤.01	Significant
AS	3.47	≤.01	Significant
MN	1.94	.05	Significant
SOL	0.10	.92	Not Significant
PCB	1.53	.13	Not significant

(Significant at $\alpha \leq .05$)

Table 3.6 Correlation Coefficients (r) for Parameters in Sediment - Lake Stations

	% LOI	TP	TKN	TOC	Cu	Cr	Hg	Fe	Pb	Zn	Mn	SOL	PCB	SILT	CLAY	SAND	CSIL	FSAND	Cd
% LOI	1.00																		
TP	0.54	1.00																	
TKN	0.93	0.63	1.00																
TOC	0.84	0.47	0.89	1.00															
Cu	0.66	0.70	0.75	0.79	1.00														
Cr	0.64	0.90	0.72	0.66	0.90	1.00													
Hg	0.65	0.70	0.70	0.71	0.82	0.80	1.00												
Fe	0.81	0.66	0.78	0.72	0.67	0.72	0.71	1.00											
Pb	0.73	0.68	0.77	0.82	0.87	0.84	0.90	0.77	1.00										
Zn	0.75	0.82	0.80	0.77	0.88	0.93	0.86	0.83	0.93	1.00									
Mn	0.73	0.50	0.72	0.65	0.55	0.55	0.52	0.90	0.60	0.70	1.00								
SOL	0.72	0.80	0.81	0.76	0.84	0.86	0.87	0.68	0.88	0.90	0.54	1.00							
PCB	0.56	0.73	0.60	0.57	0.77	0.79	0.83	0.59	0.79	0.82	0.39	0.81	1.00						
SILT	0.77	0.44	0.82	0.83	0.73	0.61	0.69	0.80	0.75	0.74	0.74	0.64	0.53	1.00					
CLAY	0.72	0.40	0.75	0.78	0.69	0.59	0.64	0.77	0.79	0.70	0.61	0.62	0.49	0.82	1.00				
SAND	-0.52	-0.52	-0.54	-0.46	-0.54	-0.61	-0.47	-0.51	-0.51	-0.57	-0.45	-0.58	-0.51	-0.40	-0.37	1.00			
CSIL	0.37	0.24	0.33	0.36	0.23	0.20	0.18	0.45	0.13	0.24	0.53	0.13	0.12	0.40	0.11	0.03	1.00		
FSAND	-0.46	-0.40	-0.50	-0.45	-0.52	-0.51	-0.54	-0.59	-0.52	-0.54	-0.55	-0.50	-0.30	-0.54	-0.46	0.49	-0.24	1.00	
Cd	0.64	0.62	0.73	0.67	0.81	0.75	0.71	0.56	0.72	0.71	0.42	0.73	0.68	0.59	0.59	-0.45	0.21	-0.44	1.00

CRITICAL VALUE (2-tail, x < or = to 0.05) = +/- 0.30

N = 44

Table 3.7 Correlation Coefficients (r) for Parameters in Sediment - River Stations

	% LOI	TP	TKN	Cu	Cr	Hg	Fe	Pb	Zn	Mn	SOL	PCB	SILT	CLAY	SAND	CSIL	FSAND	Cd
% LOI	1.00																	
TP	0.24	1.00																
TKN	0.79	0.46	1.00															
Cu	0.88	0.41	0.75	1.00														
Cr	0.77	0.46	0.66	0.83	1.00													
Hg	0.52	0.57	0.36	0.66	0.54	1.00												
Fe	0.63	0.30	0.40	0.65	0.90	0.39	1.00											
Pb	0.85	0.47	0.65	0.90	0.93	0.71	0.82	1.00										
Zn	0.81	0.41	0.50	0.88	0.86	0.80	0.78	0.95	1.00									
Mn	0.70	0.16	0.43	0.69	0.88	0.35	0.95	0.81	0.78	1.00								
SOL	0.74	0.50	0.61	0.85	0.82	0.71	0.75	0.89	0.87	0.73	1.00							
PCB	0.50	0.49	0.31	0.71	0.49	0.78	0.32	0.63	0.74	0.37	0.58	1.00						
SILT	0.71	0.28	0.92	0.74	0.59	0.31	0.28	0.57	0.44	0.34	0.57	0.27	1.00					
CLAY	0.77	0.01	0.60	0.65	0.49	0.28	0.41	0.51	0.50	0.55	0.53	0.36	0.59	1.00				
SAND	-0.19	-0.47	-0.49	-0.26	-0.43	0.08	-0.41	-0.28	-0.12	-0.34	-0.36	-0.05	-0.38	-0.11	1.00			
CSIL	0.41	0.54	0.61	0.54	0.40	0.56	0.10	0.47	0.38	0.11	0.40	0.35	0.61	0.22	-0.01	1.00		
FSAND	-0.49	-0.43	-0.67	-0.58	-0.60	-0.23	-0.50	-0.51	-0.43	-0.48	-0.57	-0.23	-0.63	-0.37	0.70	-0.20	1.00	
Cd	0.28	0.56	0.38	0.49	0.26	0.60	0.06	0.37	0.39	0.14	0.42	0.76	0.29	0.25	-0.18	0.49	-0.21	1.00

CRITICAL VALUE (2-tail, x < or = to 0.05) = +/- 0.43

N = 21

Table 3.8: Summary and Significance of Correlations Between Parameters in Lake and Rivers Stations

	$r > 0.7$		$0.5 < r < 0.7$		$r < 0.5$	
	Lake	Rivers	Lake	Rivers	Lake	Rivers
LOI	TKN,TOC,Sol,Fe,Mn,Pb,Zn	TKN,Sol,Mn,Pb,Zn,Cn,Cr	Cu,Cr,Hg,TP,Cd,PCB	Fe,Mn,Hg,PCB		TP,Cd
TP	Sol,PCB,Zn,Cu,Cr,Hg		TKN,Pb,Fe,Cr,Mn	Hg,Sol	TOC,LOI	TKN,LOI,Cu,Fe,Zn,Mn,Pb,Cr,PCB
TKN	TOC,LOI,Sol,Fe,Mn,Pb,Cd, Cr,Cu,Hg	Cu,LOI	PCB,TP	Cr,Pb,Sol,Zn		TP,Hg,Fe,Cd,Mn,PCB
TOC	TKN,LOI,Sol,Fe,Cu,Pb,Zn,Hg	*	PCB,Mn,Zn,Cr,Cd	*		*
Cu	TKN,TOC,Sol,Zn,Pb,Cr,Cd,Hg,TP	TKN,LOI,Sol,Pb,Zn,Cr,PCB	LOI,Fe,Mn	Hg,Fe,Mn		TP,Cd
Cr	TKN,Sol,Fe,Cu,Zn,TP,Hg, Pb,Cd,PCB	LOI,Sol,Fe,Mn,Pb,Zn,Cu	LOI,TOC,Mn	TKN,Hg		PCB,TP,Cd
Hg	TKN,TOC,Sol,Pb,Zn,Cu,Cr, Cd,Fe,TP,PCB	PCB,Sol,Zn,Pb	LOI,Mn	TP,Cu,Cr,Cd		Mn,Fe,TKN,TOC
Fe	TKN,LOIMn,Pb,Zn	Sol,Mn,Cr,Pb,Zn	PCB,Sol,TP,Cd,TOC	LOI,Cu		PCB,HG,TKN,TP,Cr
Pb	TOC,TKN,Sol,LOI,CU,Hg,Zn, Cd,Cr,Fe,PCB	LOI,Sol,Fe,Mn,Cu,Cr,An,Hg	TP,Mn	PCB,TKN		TP,Cd
Zn	TKN,TOC,LOI,Sol,Cu,Cr,Pb, Hg,TP,Fe,Cd,Mn,PCB	Sol,LOI,Cu,Pb,Cr,Hg,Fe, Mn,PCB		TKN		TP,Cd
Cd	TKN,Sol,Cu,Cr,Hg,Pb,Zn	PCB	LOI,TP,TOC,Fe,PCB	TP,Hg	Mn	LOI,TKN,Cu,Sol,Mn,Cr,Zn,Fe,Pb
Mn	TKN,LOI,Fe,Zn	LOI,Sol,Fe,Cr,Pb,Zn	TKN,TOC,Pb,Sol,TP,Cu,Hg	Cu	PCB,Cd	TP,TKN,Hg,PCB,Cd
Sol.	TKN,TOC,LOI,Pb,ZnHg,Cr,Cu,TP, Cd,PCB	LOI,Fe,Mn,Hg,Pb,Zn,Cu,Cr	Fe,Mn	TKN,PCB,Pb		TP,Cd
PCB	Cu,Cr,Pb,Zn,Hg,TP,Sol.	Cu,Hg,Zn,Cd	LOI,TKN,TOC,Fe,Cd	Pb,Sol	Mn	LOI,TP,TKN,Cr,Fe,Mn

* = No Data $r > 0.7$ (Significant Correlation) $0.5 < r < 0.7$ (Good Correlation) $r < 0.5$ (Weak Correlation)

LOI, TKN and TOC are highly correlated in the lake stations. Since these parameters are indicative of the organic content of the sediment, they would be expected to show strong inter-relationships. The lake stations show a remarkable degree of relationship between most of the parameters. The underlying factor in this relationship appears to be the organic content of sediment, especially the solvent extractable parameter. Iron and manganese are highly correlated with each other in both the rivers and lake stations. This is reflective of their similar chemistry and widespread occurrence in nature (Dayal et al, 1983). Both of these metals are important "carrier particles" for other metals. However, only lead and zinc in the lake and rivers and chromium in the rivers, show a strong association with iron and manganese.

It appears that the organic "carrier particles" are more effective in adsorbing contaminants than iron and manganese which are themselves strongly associated with the organic fraction. (This will be discussed in further detail in the section under sequential extraction).

PCBs show a close relationship with solvent extractables and metals at the lake stations and to some extent in the river stations although the correlation between PCB and solvent extractables is weaker in the river stations.

In general, the interrelationships among parameters are stronger in the lake stations compared with the river stations. The hydrodynamics of the river system may be a major influence in the distribution of material in sediments.

As shown in Tables 3.6 and 3.7, most of the chemical parameters are associated with the silt and clay sediment fractions.

Correlation coefficients were also calculated for stations within the various study locations in an attempt to identify common sources of the parameters measured. In many cases, the number of stations were too small to provide firm conclusions. However, parameters at stations in the St. Marys River (Table 3.9) and the Toronto East Headland (Table

Table 3.9 Correlation Coefficients (r) for Parameters in Sediment - St. Mary's River

	% LOI	TP	TKN	Cu	Cr	Hg	Fe	Pb	Zn	Mn	SOL	PCB	FSAN	SAND	CSIL	SILT	CLAY
% LOI	1.00																
TP	0.61	1.00															
TKN	0.78	0.94	1.00														
Cu	0.86	0.89	0.92	1.00													
Cr	0.96	0.69	0.80	0.93	1.00												
Hg	0.91	0.85	0.92	0.98	0.96	1.00											
Fe	0.93	0.42	0.57	0.77	0.94	0.82	1.00										
Pb	0.96	0.71	0.84	0.94	0.97	0.94	0.89	1.00									
Zn	0.96	0.62	0.75	0.90	0.99	0.93	0.96	0.97	1.00								
Mn	0.89	0.31	0.47	0.69	0.89	0.74	0.99	0.84	0.93	1.00							
SOL	0.85	0.77	0.79	0.97	0.94	0.92	0.84	0.93	0.93	0.78	1.00						
PCB	0.72	0.71	0.76	0.87	0.78	0.81	0.68	0.82	0.82	0.63	0.87	1.00					
FSAN	-0.61	-0.95	-0.93	-0.89	-0.72	-0.86	-0.44	-0.76	-0.65	-0.34	-0.77	-0.72	1.00				
SAND	-0.54	-0.63	-0.62	-0.77	-0.64	-0.64	-0.50	-0.74	-0.65	-0.47	-0.81	-0.81	0.71	1.00			
CSIL	0.54	0.90	0.86	0.75	0.60	0.76	0.32	0.60	0.49	0.20	0.60	0.40	-0.88	-0.40	1.00		
SILT	0.58	0.96	0.94	0.84	0.65	0.81	0.35	0.70	0.56	0.24	0.70	0.61	-0.97	-0.63	0.95	1.00	
CLAY	0.84	0.35	0.54	0.61	0.83	0.76	0.88	0.73	0.83	0.85	0.60	0.49	-0.39	-0.16	0.35	0.30	1.00

CRITICAL VALUE (2-tail, x < or = to 0.05) = +/- 0.75

N = 7

Table 3.10 Correlation Coefficients (r) for Parameters in Sediment - Toronto East Headland

	% LOI	TP	TKN	Cu	Cr	Hg	Fe	Pb	Zn	Mn	SOL	PCB	FSAN	SAND	CSIL	SILT	CLAY
% LOI	1.00																
TP	0.67	1.00															
TKN	0.99	0.71	1.00														
Cu	0.97	0.74	0.99	1.00													
Cr	0.90	0.85	0.93	0.96	1.00												
Hg	0.92	0.46	0.90	0.91	0.81	1.00											
Fe	0.96	0.70	0.97	0.98	0.94	0.92	1.00										
Pb	0.91	0.70	0.93	0.96	0.94	0.91	0.98	1.00									
Zn	0.94	0.73	0.96	0.99	0.95	0.90	0.95	0.96	1.00								
Mn	0.95	0.61	0.94	0.92	0.88	0.94	0.96	0.91	0.88	1.00							
SOL	0.68	0.36	0.69	0.62	0.56	0.58	0.72	0.61	0.52	0.77	1.00						
PCB	0.90	0.47	0.89	0.86	0.76	0.86	0.89	0.81	0.79	0.94	0.88	1.00					
FSAN	-0.83	-0.60	-0.81	-0.82	-0.84	-0.83	-0.78	-0.74	-0.79	-0.87	-0.49	-0.75	1.00				
SAND	-0.34	0.16	-0.21	-0.16	0.01	-0.45	-0.17	-0.14	-0.16	-0.30	-0.02	-0.24	0.27	1.00			
CSIL	0.48	0.72	0.55	0.66	0.75	0.49	0.64	0.72	0.71	0.50	0.19	0.39	-0.45	0.32	1.00		
SILT	0.90	0.53	0.90	0.93	0.86	0.97	0.91	0.91	0.93	0.93	0.57	0.87	-0.86	-0.28	0.63	1.00	
CLAY	0.90	0.79	0.94	0.97	0.99	0.84	0.96	0.97	0.96	0.89	0.60	0.79	-0.80	0.03	0.76	0.89	1.00

CRITICAL VALUE (2-tail, x < or = to 0.05) = +/- 0.70

N = 8

3.10) show a high degree of interrelationship suggesting that in addition to the parameter association with particular "carrier particles", there appears to be common sources of contaminants in each of the these two areas respectively.

3.2 Sediment-Sequential Extraction of Metals

Results of the sequential chemical extractions (on the <63 μm sediment) for each of the six geochemical phases (IW-interstitial water, F1-cation exchangeable, F2-easily reducible, F3-organic sulphide, F4-moderately reducible and Res-residual) are provided in Tables in Volume IV of this report series. The tables provide the concentrations of the metal (As, Zn, Cu, Cd, Mn, Fe, Pb) in each of the phases and the total metal concentrations which were obtained by summing the geochemical phases (i.e. TRSUM = 1W + F1 + F2 + F3 + F4 + RES).

Table 3.11 provides a summary of the geochemical phases with the highest concentration of each metal. At most stations, As, Cd, Cu, Pb and Zn showed the highest concentrations in the F3 (organic/sulphide) phase. Manganese was concentrated in the F3 phase at about half of the stations and in the residual phase at the other half. Iron was found mainly in the residual phase.

3.2.1 Metal Distribution Among The Geochemical Phases Of Sediment

Summary statistics for the sequential extraction results for each of the study locations are provided in Tables 3.12-3.17. The information in the tables includes metals in each geochemical phase (average concentration and % of total metal), TRSUM (sum of individual phases) and potentially available metal (IW-F4) for each of the study locations. Arsenic will not be discussed in this section because of the small data set.

The proportion of metals in the various phases provides an indication of the influence of the different "carrier particles" in adsorbing metals. Metals in the residual phase are normally associated with detrital minerals, refractory organics and resistant sulphides (Tessier et al.,

TABLE 3.11: SUMMARY OF THE GEOCHEMICAL PHASES WITH THE HIGHEST METAL CONTENT

METAL	LARGEST LEVEL (L)	NO. OF STATIONS WITH L LARGER THAN OTHERS	TOTAL NO. OF STATIONS
AS	F3	32	40
CD	F3	73	87
CU	F3	77	87
FE	RES	69	87
PB	F3	84	87
MN	F3 RES	44 43	87
ZN	F3	74	87

Table: 3.12 Summary Statistics for Geochemical Distribution of Copper According to Study Locations

Study Locations	IW		F1		F2		F3		F4		Potentially Available Metal (ΣIW - F4)		Residual		Total
	$\bar{X}$	%	$\bar{X}$	%	$\bar{X}$	%	$\bar{X}$	%	$\bar{X}$	%	$\bar{X}$	%	$\bar{X}$	%	($\Sigma\bar{X}$)
WINDERMERE BASIN	0.050	0.026	8.480	4.482	0.002	0.001	131.224	69.353	31.388	16.589	171.144	90.451	18.068	9.549	189.212
O/S HAMIL. HARBOUR	0.020	0.062	4.106	12.767	0.002	0.006	20.874	64.903	2.922	9.085	27.924	86.823	4.238	13.177	32.162
HUMBER BAY	0.047	0.033	3.882	2.702	0.047	0.033	104.212	72.531	12.525	8.717	120.071	83.569	22.951	15.974	143.679
TORONTO HARBOUR	0.043	0.060	2.632	3.690	0.002	0.003	46.602	65.327	3.245	4.549	52.524	73.629	18.812	26.371	71.336
EASTHEADLAND	0.009	0.010	0.211	0.237	1.596	1.792	63.107	70.852	6.017	6.755	70.931	79.636	18.120	20.344	89.069
ASHBRIDGES BAY	0.041	0.024	5.570	3.205	0.002	0.001	87.600	50.408	19.170	11.031	112.383	64.669	61.400	35.331	173.783
TOR. E. WATERFRONT	0.026	0.110	3.597	15.216	0.002	0.008	10.508	44.452	1.064	4.501	15.196	64.284	8.440	35.704	23.639
FRENCHMAN BAY	0.009	0.016	9.882	17.192	0.002	0.003	32.924	57.278	8.476	14.746	51.293	89.235	6.188	10.765	57.481
ST.CLAIR RIVER	0.005	0.015	0.394	1.175	0.085	0.254	25.891	77.231	1.197	3.571	27.567	82.231	5.950	17.748	33.524
NIAGARA RIVER	0.005	0.006	0.094	0.106	0.158	0.178	72.360	81.300	3.189	3.583	75.800	85.165	13.195	14.825	89.004
ST. MARY'S RIVER	0.005	0.006	0.263	0.306	0.187	0.218	61.058	71.017	4.824	5.611	66.330	77.149	19.631	22.833	85.976
ST. LAWRENCE RIVER	0.005	0.014	0.109	0.304	0.109	0.304	24.456	68.294	2.847	7.950	27.522	76.856	8.277	23.114	35.810

$\bar{X}$ - Mean Concentration (ppm)
% - % of Total Metal (i.e. $\Sigma\bar{X}$)

Table: 3.13 Summary Statistics for Geochemical Distribution of Cadmium According to Study Locations

Study Locations	IW		F1		F2		F3		F4		Potentially Available Metal (ΣIW -F4)		Residual		Total
	$\bar{X}$	%	$\bar{X}$	%	$\bar{X}$	%	$\bar{X}$	%	$\bar{X}$	%	$\bar{X}$	%	$\bar{X}$	%	($\Sigma\bar{X}$)
WINDERMERE BASIN	0.010	0.086	0.490	4.205	0.768	6.590	6.204	53.235	1.760	15.102	9.232	79.217	2.422	20.783	11.654
O/S HAMIL. HARBOUR	0.007	0.172	0.236	5.811	0.648	15.957	1.350	33.243	0.374	9.210	2.615	64.393	1.446	35.607	4.061
HUMBER BAY	0.013	0.123	0.184	1.745	0.452	4.287	7.184	68.134	0.889	8.431	8.721	82.711	1.794	17.014	10.544
TORONTO HARBOUR	0.013	0.152	0.284	3.320	0.396	4.629	4.846	56.645	0.949	11.093	6.488	75.839	2.067	24.161	8.555
EASTHEADLAND	0.008	0.474	0.030	1.777	0.030	1.777	1.492	88.389	0.098	5.806	1.658	98.223	0.030	1.777	1.688
ASHBRIDGES BAY	0.008	0.109	0.250	3.414	0.445	6.077	3.965	54.144	0.390	5.326	5.058	69.070	2.265	30.930	7.323
TOR. E. WATERFRONT	0.008	0.176	0.222	4.896	0.430	9.484	1.527	33.679	0.179	3.948	2.365	52.161	2.169	47.839	4.534
FRENCHMAN BAY	0.005	0.062	0.418	5.151	1.274	15.699	3.840	47.320	0.674	8.306	6.211	76.537	1.904	23.463	8.115
ST.CLAIR RIVER	0.003	0.301	0.045	4.514	0.050	5.015	0.643	64.493	0.049	4.915	0.792	79.438	0.205	20.562	0.997
NIAGARA RIVER	0.003	0.086	0.052	1.486	0.052	1.486	3.253	92.969	0.086	2.458	3.447	98.514	0.052	1.486	3.499
ST. MARY'S RIVER	0.003	0.241	0.055	4.425	0.055	4.425	1.006	80.933	0.066	5.310	1.188	95.575	0.055	4.425	1.243
ST. LAWRENCE RIVER	0.003	0.232	0.066	5.112	0.066	5.112	0.968	74.981	0.066	5.112	1.171	90.705	0.120	9.295	1.291

$\bar{X}$ - Mean Concentration (ppm)

% - % of Total Metal (i.e. $\Sigma\bar{X}$)

Table: 3.14 Summary Statistics for Geochemical Distribution of Lead According to Study Locations

Location	IW		F1		F2		F3		F4		Potentially Available Metal(ΣIw - F4)		Residual		Total
	$\bar{X}$	%	$\bar{X}$	%	$\bar{X}$	%	$\bar{X}$	%	$\bar{X}$	%	$\bar{X}$	%	$\bar{X}$	%	($\Sigma\bar{X}$)
WINDERMERE BASIN	0.055	0.014	3.156	0.824	9.338	2.437	277.700	72.481	7.288	1.902	297.897	77.752	85.240	22.248	383.137
D/S HAMIL. HARBOUR	0.005	0.007	1.626	2.237	7.056	9.706	45.900	63.137	2.812	3.868	57.399	78.954	15.300	21.046	72.699
HUMBER BAY	0.021	0.010	3.075	1.455	4.989	2.361	186.625	88.321	4.403	2.084	199.112	94.231	11.972	5.666	211.303
TORONTO HARBOUR	0.047	0.014	4.344	1.282	6.725	1.985	243.490	71.859	3.049	0.900	257.655	76.039	81.190	23.961	338.845
EASTHEADLAND	0.025	0.013	0.858	0.448	3.233	1.688	173.852	90.789	9.683	5.057	187.652	97.995	3.820	1.995	191.491
ASHBRIDGES BAY	0.039	0.010	5.445	1.440	7.415	1.962	277.250	73.344	1.815	0.480	291.964	77.236	86.050	22.764	378.014
TOR. E. WATERFRONT	0.015	0.019	3.810	4.822	4.849	6.137	52.886	66.930	0.976	1.235	62.505	79.104	16.511	20.896	79.016
FRENCHMAN BAY	0.018	0.011	5.502	3.272	14.024	8.341	125.320	74.536	4.190	2.492	149.054	88.652	19.080	11.348	168.134
ST.CLAIR RIVER	0.025	0.036	0.376	0.545	0.376	0.545	66.042	95.714	0.686	0.994	67.505	97.835	1.482	2.148	68.999
NIAGARA RIVER	0.025	0.023	0.430	0.398	0.430	0.398	100.468	92.973	3.039	2.812	104.392	96.605	3.651	3.379	108.061
ST. MARY'S RIVER	0.020	0.012	0.647	0.402	0.647	0.402	141.611	87.930	8.736	5.424	151.665	94.173	9.344	5.802	161.049
ST. LAWRENCE RIVER	0.025	0.102	0.546	2.231	0.546	2.231	21.822	89.175	0.546	2.231	23.485	95.971	0.956	3.907	24.471

$\bar{X}$ - Mean Concentration (ppm)
% - % of Total Metal (i.e. $\Sigma\bar{X}$)

Table: 3.15 Summary Statistics for Geochemical Distribution of Zinc According to Study Locations

Study Locations	IW		F1		F2		F3		F4		Potentially Available Metal(ΣIW - F4)		Residual		Total
	$\bar{X}$	%	$\bar{X}$	%	$\bar{X}$	%	$\bar{X}$	%	$\bar{X}$	%	$\bar{X}$	%	$\bar{X}$	%	($\Sigma\bar{X}$)
WINDERMERE BASIN	0.590	0.041	11.488	0.807	27.898	1.960	1008.880	70.868	292.560	20.551	1341.416	94.227	82.180	5.773	1423.596
O/S HAMIL. HARBOUR	0.094	0.058	4.882	3.033	8.582	5.332	97.060	60.309	6.320	3.927	116.938	72.660	44.000	27.340	160.938
HUMBER BAY	0.073	0.012	3.428	0.563	8.705	1.429	467.190	76.682	39.541	6.490	518.925	85.174	90.554	14.863	609.254
TORONTO HARBOUR	0.133	0.032	2.426	0.587	8.578	2.077	340.910	82.555	12.252	2.967	364.299	88.219	48.650	11.781	412.949
EASTHEADLAND	0.006	0.002	0.910	0.334	5.898	2.162	144.763	53.076	34.672	12.712	186.334	68.317	86.409	31.681	272.748
ASHBRIDGES BAY	0.027	0.005	4.315	0.726	8.860	1.491	392.950	66.116	13.135	2.210	419.287	70.547	175.050	29.453	594.337
TOR. E. WATERFRONT	0.022	0.023	2.017	2.089	3.832	3.968	46.222	47.867	1.114	1.154	53.207	55.101	43.356	44.899	96.563
FRENCHMAN BAY	0.040	0.020	1.900	0.957	4.890	2.464	123.340	62.145	2.740	1.381	132.912	66.968	65.560	33.032	198.472
ST.CLAIR RIVER	0.003	0.002	0.872	0.651	1.441	1.076	95.316	71.140	4.741	3.538	102.370	76.405	31.698	23.658	133.984
NIAGARA RIVER	0.003	0.001	1.397	0.352	7.494	1.889	257.183	64.841	22.110	5.574	288.187	72.657	108.454	27.343	396.639
ST. MARY'S RIVER	0.011	0.003	2.722	0.621	38.811	8.848	307.493	70.102	18.633	4.248	367.689	83.825	70.938	16.172	438.638
ST. LAWRENCE RIVER	0.011	0.010	0.421	0.401	0.713	0.680	51.621	49.228	6.562	6.258	59.328	56.577	45.521	43.410	104.862

$\bar{X}$ - Mean Concentration (ppm)
% - % of Total Metal (i.e. $\Sigma\bar{X}$)

Table: 3.16 Summary Statistics for Geochemical Distribution of Manganese According to Study Locations

Study Locations	IW		F1		F2		F3		F4		Potentially Available Metal (ΣIW - F4)		Residual		Total
	$\bar{X}$	%	$\bar{X}$	%	$\bar{X}$	%	$\bar{X}$	%	$\bar{X}$	%	$\bar{X}$	%	$\bar{X}$	%	($\Sigma\bar{X}$)
WINDERMERE BASIN	2.248	0.359	11.038	1.762	264.060	42.154	251.478	40.146	68.788	10.981	597.612	95.402	28.800	4.598	626.412
O/S HAMIL. HARBOUR	14.096	2.246	15.698	2.501	275.720	43.929	281.022	44.774	22.070	3.516	608.606	96.966	19.004	3.028	627.646
HUMBER BAY	2.836	0.602	17.459	3.703	65.609	13.917	196.478	41.677	25.757	5.464	308.160	65.367	163.153	34.608	471.428
TORONTO HARBOUR	3.265	0.676	3.917	0.811	62.679	12.978	170.325	35.268	11.505	2.382	251.691	52.115	231.260	47.885	482.951
EASTHEADLAND	1.148	0.175	45.560	6.962	80.185	12.254	254.363	38.871	43.043	6.578	424.298	64.840	229.199	35.026	654.374
ASHBRIDGES BAY	3.705	0.788	2.450	0.521	23.715	5.042	161.455	34.329	8.995	1.913	200.320	42.592	270.000	57.408	470.320
TOR. E. WATERFRONT	2.793	0.567	1.694	0.344	32.747	6.645	102.351	20.770	9.899	2.009	149.484	30.335	343.289	69.665	492.773
FRENCHMAN BAY	3.686	0.721	5.268	1.030	128.928	25.202	255.546	49.952	14.974	2.927	408.402	79.831	103.180	20.169	511.582
ST.CLAIR RIVER	0.728	0.201	11.627	3.204	35.468	9.773	213.898	58.939	11.507	3.171	273.228	75.287	89.363	24.624	362.914
NIAGARA RIVER	1.612	0.322	27.581	5.515	76.038	15.204	175.169	35.026	14.257	2.851	294.657	58.918	204.046	40.800	500.117
ST. MARY'S RIVER	0.598	0.059	49.549	4.877	62.127	6.115	82.645	8.134	23.202	2.284	228.120	22.452	786.642	77.423	1016.028
ST. LAWRENCE RIVER	0.041	0.011	11.791	3.063	40.672	10.567	105.789	27.485	9.816	2.550	168.107	43.676	216.738	56.311	384.898

$\bar{X}$ - Mean Concentration (ppm)

% - % of Total Metal (i.e. $\Sigma\bar{X}$)

Table: 3.17 Summary Statistics for Geochemical Distribution of Iron According to Study Locations

Study Locations	IW		F1		F2		F3		F4		Potentially Available Metal (ΣIW - F4)		Residual		Total
	$\bar{X}$	%	$\bar{X}$	%	$\bar{X}$	%	$\bar{X}$	%	$\bar{X}$	%	$\bar{X}$	%	$\bar{X}$	%	($\Sigma\bar{X}$)
WINDERMERE BASIN	2.830	0.018	28.000	0.181	774.550	4.997	7109.000	45.864	0.000	0.000	3130.410	20.196	7585.800	48.940	15500.170
O/S HAMIL. HARBOUR	2.520	0.013	5.490	0.028	223.770	1.155	3544.600	18.300	0.000	0.000	891.980	4.605	15593.200	80.504	19369.590
HUMBER BAY	1.290	0.005	7.000	0.029	107.468	0.444	6429.995	26.583	588.111	2.431	7133.862	29.493	17054.964	70.508	24188.644
TORONTO HARBOUR	2.160	0.016	3.770	0.028	98.600	0.731	7164.100	53.103	0.000	0.000	2923.030	21.666	6222.400	46.122	13491.030
EASTHEADLAND	0.100	0.000	0.450	0.001	142.488	0.421	6827.429	20.175	1665.584	4.922	8636.056	25.519	25205.675	74.481	33841.753
ASHBRIDGES BAY	1.260	0.011	3.220	0.028	34.660	0.300	4722.500	40.822	0.000	0.000	823.500	7.118	6807.000	58.840	11568.630
TOR. E. WATERFRONT	0.430	0.002	1.200	0.007	34.360	0.199	3053.330	17.724	0.000	0.000	1832.350	10.636	14138.110	82.067	17227.420
FRENCHMAN BAY	1.710	0.006	5.580	0.021	118.280	0.435	12531.800	46.098	0.000	0.000	5073.810	18.664	14527.600	53.440	27184.970
ST.CLAIR RIVER	0.320	0.002	1.938	0.013	97.966	0.666	4159.542	28.297	516.242	3.512	4776.013	32.491	10082.866	68.594	14699.357
NIAGARA RIVER	12.570	0.039	0.200	0.001	193.000	0.602	6549.300	20.430	631.100	1.969	7386.200	23.041	22731.900	70.912	32056.600
ST. MARY'S RIVER	0.090	0.000	4.091	0.006	504.843	0.791	5875.142	9.210	1195.853	1.875	7580.014	11.883	56208.450	88.117	63788.641
ST. LAWRENCE RIVER	0.010	0.000	2.695	0.011	25.397	0.100	4115.364	16.132	680.857	2.669	4824.325	18.912	20685.444	81.088	25509.794

$\bar{X}$ - Mean Concentration (ppm)
% - % of Total Metal (i.e. $\Sigma\bar{X}$)

1979). Metals in this phase are chemically stable under normal environmental conditions and can be considered biologically unavailable. The potentially available metal (IW-F4) can be considered to have originated mainly from anthropogenic sources (Tessier, et al., 1979). Table 3.12 shows the geochemical distribution of copper (Cu) among the study locations. For most areas, over 75% of the Cu was in potentially available forms. The two exceptions were Ashbridges Bay and Eastern Toronto Waterfront where 35% was in the residual form. Most of the Cu outside the residual phase was associated with the F3 (organic/sulphide fraction) phase. Concentrations in the IW and F2 phases were negligible. The F1 (cation exchangeable) phase showed appreciable amounts of Cu in sediment from Eastern Toronto Waterfront, outside Hamilton Harbour and Frenchman Bay. This phase consists of the easily available fraction which is in dynamic equilibrium with the surrounding water. The F4 (moderately reducible, Fe/Mn oxyhydroxide fraction) phase contained significant amounts of Cu, suggesting that next to organic material, the metal hydrous oxides are the most important "carrier particles" for copper.

Over 90% of the cadmium (Cd) in the St. Marys River, St. Lawrence River and Niagara River and the East Toronto Headland was in potentially available forms. The lowest value of available cadmium was noted for sediment from Eastern Toronto Waterfront, where almost 50% was bound up in the residual fraction (Table 3.13). Appreciable amounts of cadmium were noted in the F1, F2 and F4 phases, but the bulk of the available Cd was in the F3 phase (organic/sulphide fraction).

More than 75% of lead (Pb) was in the potentially available forms for all stations (Table 3.14). In Humber Bay, Toronto East Headland and the interconnecting channels, over 90% of the Pb was in available forms. Most of the available Pb was associated with the F3 phase (organic/sulphide fraction) with extremely low levels in the other available (non-residual) fractions.

A significant proportion of the zinc (Zn) in the St. Lawrence River and Eastern Toronto Waterfront sediments was bound up in the residual fraction (Table 3.15). In general, most of the Zn was associated with

the F3 phase. However, at the Toronto East Headland and Windermere Basin appreciable amounts of Zn were associated with the Fe/Mn oxyhydroxide phase. Zinc concentrations in the other non-residual phases were negligible.

Over 50% of the manganese (Mn) in Ashbridges Bay, Eastern Toronto Waterfront, St. Marys River and St. Lawrence River was concentrated in the residual phase (Table 3.16). Toronto Harbour and Niagara River also showed significant proportions (40%) of Mn in the residual phase. Unlike the metals discussed earlier, a considerable proportion of Mn was found in the F2 phase (easily reducible fraction) which represents mainly the Mn oxyhydroxides. Only the St. Clair River sediments had more than 50% Mn in the F3 phase.

The bulk of Fe was found in the residual phase, with most of the available Fe in the F3 phase.

With the exception of Fe and Mn, most of the potentially available metals were concentrated in the F3 phase (organic/sulphide fraction). This information agrees quite well with the results obtained through the correlation matrix on the bulk chemistry data, where good correlations were noted between the metals and the organic matter content of sediment and poor correlations between the other metals and Fe and Mn.

Fine organic matter has a large surface area to volume ratio and can therefore, in proportion to its volume, adsorb considerably greater amounts of metals. In addition, the other non-residual "carrier particles" appeared to be themselves associated with the organic/sulphide fraction, making this fraction the most important geochemical phase with which the metals were associated.

The largest fraction of Fe and to some extent Mn, was held in the residual phase. The sediments of Eastern Toronto Waterfront showed higher residual values for most metals compared with sediments from other locations, perhaps due to the lower organic matter content and higher mineral content of sediments from this area.

With the exception of Fe and Mn, most of the metals are in potentially available forms. Release from sediments however, will depend on changes in the physico-chemical factors (Eh, pH) which regulate the metal chemistry.

3.3 Biological Results

Of the 87 stations sampled during the 1983 survey, sediment from 49 stations provided adequate amounts of benthic tissue for chemical analyses. At 42 of the 49 stations, oligochaetes were the predominant group of organisms found and was comprised mainly of *Limnodrilus hoffmeisteri* and *Tubifex tubifex*. At the other 7 stations where adequate amounts of benthic tissue were obtained, there were abundances of organisms other than oligochaetes. These included mayfly nymphs at stations 50 and 51 in the upper St. Marys River (Figure 2.8) and station 64 in the St. Clair River (Figure 2.9); amphipods at stations 356 and 357 in the St. Lawrence River (Figure 2.11); chironomids at station 360 in the St. Lawrence River and station 2084 on the Eastern Toronto Waterfront (Figure 2.6).

Sufficient biomass for chemical analysis could not be obtained at 38 stations because of one or more of the following:

1. The substrate was unsuitable (e.g. sandy substrate) as benthic habitat. As a result, benthic densities were low.

2. There were high diversities and low densities of organisms which made it difficult to obtain enough organisms from any one taxon for analysis.

3. In areas where the sediment was high in organic matter, the organic debris created difficulties in sieving by clogging the mesh of the sieve. This, coupled with low organism density made sorting of the organisms difficult.

4. Certain areas were devoid of organisms, possibly the result of toxic bottom conditions since the sediment from these areas showed high levels of chemical contamination.

Chemical analyses for metals, PCBs and organochlorine pesticides (PCB/OC) required approximately 10 - 15 gms of tissue. When less than 10 gms were obtained, analyses were carried out first for the metals (except Hg), then Hg followed by PCB/organochlorine pesticides (scan). Based on this scheme, data on metal levels in oligochaetes were obtained at 42 stations, Hg at 38 and PCB/OC at 22 stations.

Arsenic was not included on the initial list of metals to be analyzed but was introduced during the late stages of the Phase 1 studies . As a result, data on arsenic levels in benthic tissue were only obtained for 10 stations. Detectable levels of the other metals were obtained at all stations for which analyses were carried out (summary statistics are provided in Table 3.18). Among the pesticides; DDT, mirex, heptachlor epoxide, dieldrin, endrin and the endosulfan isomers were not detected in benthic tissue. Summary statistics for PCBs and the pesticides that bioaccumulated in benthic tissue are provided in Table 3.19.

3.3.1 The Relationship Between Contaminant Levels in Benthic Organisms and Sediment

3.3.1.1 PCBs and Organochlorine Pesticides.

Table 3.20 shows the levels of PCB and pesticides in benthic tissue and sediment and the ratio of the tissue/sediment values referred to as bioconcentration factors.

Significant bioaccumulation of pesticides by oligochaetes were noted at certain locations. These included stations in the vicinity of the Toronto Main Sewage Treatment Plant outfall (2101, 2102 and 2103, Figure 2.5); Toronto Harbour (1346, 1352, 1354, 1362, 1365, 1366 and 1379, Figure 2.4); Humber Bay (2330, 2331, 2334, 2335 and 2369, Figure 2.3) and one station directly outside Hamilton Harbour (2097, Figure 2.2).

The sediment from these stations showed very low levels of pesticides and in many cases, levels were below analytical detection limits (a value of half the detection limits has been substituted in these cases).

TABLE 3.18: SUMMARY STATISTICS FOR METALS IN BENTHIC TISSUE ($\mu g/g$, dry wt.)

PARAMETERS	MEAN	STANDARD DEVIATION	MINIMUM	MAXIMUM
As	5.3	7.4	0.7	21.6
Cd	0.3	0.2	0.1	1.2
Cu	36.1	19.9	9.6	82.0
Fe	3498.4	7065.9	104.2	41655.7
Hg	0.3	0.1	0.1	0.5
Mn	31.5	35.7	1.2	183.7
Pb	9.5	16.0	0.1	60.6
Zn	216.3	128.0	62.9	663.4

TABLE 3.19: SUMMARY STATISTICS FOR PCB AND PESTICIDES IN BENTHIC TISSUE (ng/g, dry wt.)

PARAMETERS	MEAN	STANDARD DEVIATION	MINIMUM	MAXIMUM
DDD	135.12	135.11	38.70	459.40
Chlordane	78.29	45.28	9.52	193.20
Lindane	48.62	43.29	9.71	147.23
A-BHC	28.94	22.20	9.69	106.27
DDE	119.57	69.65	58.39	328.90
Aldrin	47.36	53.17	16.43	204.37
Heptachlor	32.87	39.90	12.85	158.95
HCB	116.62	101.47	26.06	453.44
PCB	1030.00	640.00	130.00	1970.00

Table 3.20 PCB and Pesticides Residues in Sediment And Benthic Tissue
And Bioconcentration Factors (ratio of Benthic Tissue conc./Sediment conc.)

	** PCB **			** PP,DDD **			** ALDRIN **		
Station	Sediment (ng/g dry wt.)	Benthic Tissue Corrected For Gut Content (ng/g dry wt.)	BCF	Sediment (ng/g dry wt.)	Benthic Tissue Corrected For Gut Content (ng/g dry wt.)	BCF	Sediment (ng/g dry wt.)	Benthic Tissue Corrected For Gut Content (ng/g dry wt.)	BCF
1346	1300	1450	1	46.00	459.40	10	0.50	38.86	78
1352	590	1330	2	2.50	38.70	15	0.50	25.81	52
1354	350	1150	3	--	--	--	--	--	--
1357	150	1090	7	--	--	--	--	--	--
1362	110	580	5	2.50	68.45	27	--	--	--
1365	120	1140	10	2.50	138.94	56	0.50	25.85	52
1366	180	1470	8	20.00	124.52	6	0.50	29.22	58
1371	290	120	0	--	--	--	--	--	--
1379	30	260	9	--	--	--	--	--	--
2034	300	700	2	--	--	--	--	--	--
2082	10	260	26	--	--	--	--	--	--
2083	10	130	13	--	--	--	--	--	--
2089	1010	1640	2	--	--	--	--	--	--
2090	3090	1320	0	--	--	--	--	--	--
2097	10	1810	181	--	--	--	0.50	16.43	33
2101	10	250	25	--	--	--	--	--	--
2102	10	320	32	--	--	--	--	--	--
2103	10	1530	153	--	--	--	0.50	204.37	409
2330	190	1520	8	2.50	99.81	40	0.50	38.64	77
2331	120	1780	15	20.00	90.08	5	0.50	45.10	90
2334	30	1710	57	2.50	61.05	24	0.50	22.49	45
2335	30	1970	66	--	--	--	0.50	51.59	103
2369	--	--	--	--	--	--	0.50	22.63	45

-- Not Detected in Benthic Organisms

Bioconcentration Factors (BCF) Were Rounded Off To The Nearest Whole Number

Table 3.20 (cont'd) PCB and Pesticides Residues in Sediment And Benthic Tissue And Bioconcentration Factors (ratio of Benthic Tissue)

Station	** LINDANE **			** HCB **			** PP,DDE **		
	Sediment (ng/g dry wt.)	Benthic Tissue Corrected For Gut Content (ng/g dry wt.)	BCF	Sediment (ng/g dry wt.)	Benthic Tissue Corrected For Gut Content (ng/g dry wt.)	BCF	Sediment (ng/g dry wt.)	Benthic Tissue Corrected For Gut Content (ng/g dry wt.)	BCF
1346	0.50	9.71	19	2.00	42.09	21	0.50	74.50	147
1352	0.50	16.13	32	0.50	68.17	136	0.50	87.13	174
1354	0.50	75.02	150	--	--	--	--	--	--
1357	--	--	--	2.00	26.06	13	0.50	65.23	130
1362	0.50	78.28	157	0.50	104.37	209	--	--	--
1365	--	--	--	0.50	67.86	136	0.50	84.02	168
1366	--	--	--	0.50	81.17	162	0.50	129.88	260
1371	--	--	--		--	--	--	--	--
1379	--	--	--	1.00	42.38	42	--	--	--
2034	0.50	52.38	105	0.50	288.13	576	--	--	--
2082	0.50	19.76	40		--	--	--	--	--
2083	0.50	19.71	39		--	--	--	--	--
2089	--	--	--	0.50	38.75	78	0.50	67.82	136
2090	--	--	--	0.50	109.21	218	0.50	86.36	173
2097	--	--	--	0.50	157.86	316	96.00	213.78	2
2101	0.50	55.05	110	0.50	453.44	907	--	--	--
2102	0.50	147.23	294	0.50	55.61	111	0.50	98.15	196
2103	0.50	12.97	26	0.50	123.27	247	0.50	58.39	117
2330	--	--	--	3.00	80.49	27	5.00	132.00	26
2331	--	--	--	0.50	83.77	168	0.50	128.87	258
2334	--	--	--	0.50	154.32	309	--	--	--
2335	--	--	--	0.50	148.32	297	--	--	--
2369	--	--	--	0.50	90.53	181	--	--	--

-- Not Detected in Benthic Organisms

Bioconcentration Factors (BCF) Were Rounded Off To The Nearest Whole Number

Table 3.20 (cont'd) PCB and Pesticides Residues in Sediment And Benthic Tissue
And Concentration Factors (ratio of Benthic Tissue)

Station	** A-BHC **			** CHLORDANE **			** HEPTACHLOR **		
	Sediment (ng/g dry wt.)	Benthic Tissue Corrected For Gut Content (ng/g dry wt.)	BCF	Sediment (ng/g dry wt.)	Benthic Tissue Corrected For Gut Content (ng/g dry wt.)	BCF	Sediment (ng/g dry wt.)	Benthic Tissue Corrected For Gut Content (ng/g dry wt.)	BCF
1346	0.50	12.95	26	8.00	106.80	13	0.50	25.91	52
1352	0.50	25.81	52	2.00	80.66	40	0.50	19.36	39
1354	0.50	16.30	33	2.00	45.63	23	0.50	78.28	157
1357	--	--	--	--	--	--	0.50	13.04	26
1362	0.50	16.30	33	2.00	88.03	44	--	--	--
1365	0.50	19.39	39	2.00	77.54	39	0.50	16.15	32
1366	0.50	19.48	39	16.00	84.19	5	0.50	19.48	39
1371	--	--	--	--	--	--	--	--	--
1379	0.50	19.56	39	2.00	32.58	16	--	--	--
2034	--	--	--	--	--	--	--	--	--
2082	--	--	--	--	--	--	--	--	--
2083	--	--	--	--	--	--	--	--	--
2089	--	--	--	18.50	9.52	0	--	--	--
2090	0.50	22.48	45	--	--	--	0.50	12.85	26
2097	0.50	36.17	72	--	--	--	0.50	13.14	26
2101	0.50	25.90	52	2.00	25.89	13	--	--	--
2102	0.50	35.98	72	2.00	85.03	43	--	--	--
2103	0.50	32.43	65	2.00	100.54	50	0.50	158.95	318
2330	0.50	106.27	213	2.00	193.20	97	0.50	19.32	39
2331	0.50	12.88	26	11.00	128.80	12	0.50	19.33	39
2334	0.50	41.78	84	4.00	57.83	14	0.50	25.71	51
2335	0.50	38.69	77	--	--	--	0.50	25.79	51
2369	0.50	9.69	19	9.00	58.11	6	0.50	12.93	26

-- Not Detected in Benthic Organisms

Bioconcentration Factors (BCF) Were Rounded Off To The Nearest Whole Number

A common characteristic of several of the stations at which pesticide bioaccumulation by oligochaetes was noted, was their proximity to discharges. The station outside Hamilton Harbour is influenced by discharges from the Harbour; the Humber Bay stations are influenced by discharges from the Humber River, Mimico Creek, the Humber STP and storm sewers (Figure 3.2); stations in Toronto Harbour are influenced by various storm sewers (Figure 3.2) and the Don River. Stations 2101, 2102 and 2103 are in close proximity to the Toronto Main STP discharge.

The detection of several pesticides in biota and the proximity of the stations to discharge sources suggest that although the concentrations of these pesticides in sediment were low, there may be continuous inputs of low levels of these pesticides which accumulate in the tissues of benthic organisms that feed on the incoming material. This aspect will be addressed in the discussion section that follows.

3.3.1.2 Metals

Table 3.21 shows the level of metals in sediment and biota and the respective bioconcentration factors. The sediment metal values used in these tables were the "available" metal concentrations (IW-F4) obtained from the sequential extraction data. The stations where biota bioconcentrated contaminants are shown in Figure 3.3.

Manganese (Mn), cadmium (Cd) and lead (Pb) levels were extremely low in benthic tissues compared with the sediment values. In some cases, the Pb levels in benthic tissue were so low that gut correction resulted in negative values (Table 3.21). This would indicate that most of the wet weight values for Pb in biota were associated with the sediment of the gut.

The levels of copper in benthic tissue exceeded the levels in sediment at 15 of the 42 stations (i.e. concentration factors >1).

Among the biologically essential metals, Zn showed the highest uptake values relative to sediment levels. The body burden values showed wide variation ranging from 62 ppm to 671 ppm, with 90% of the samples

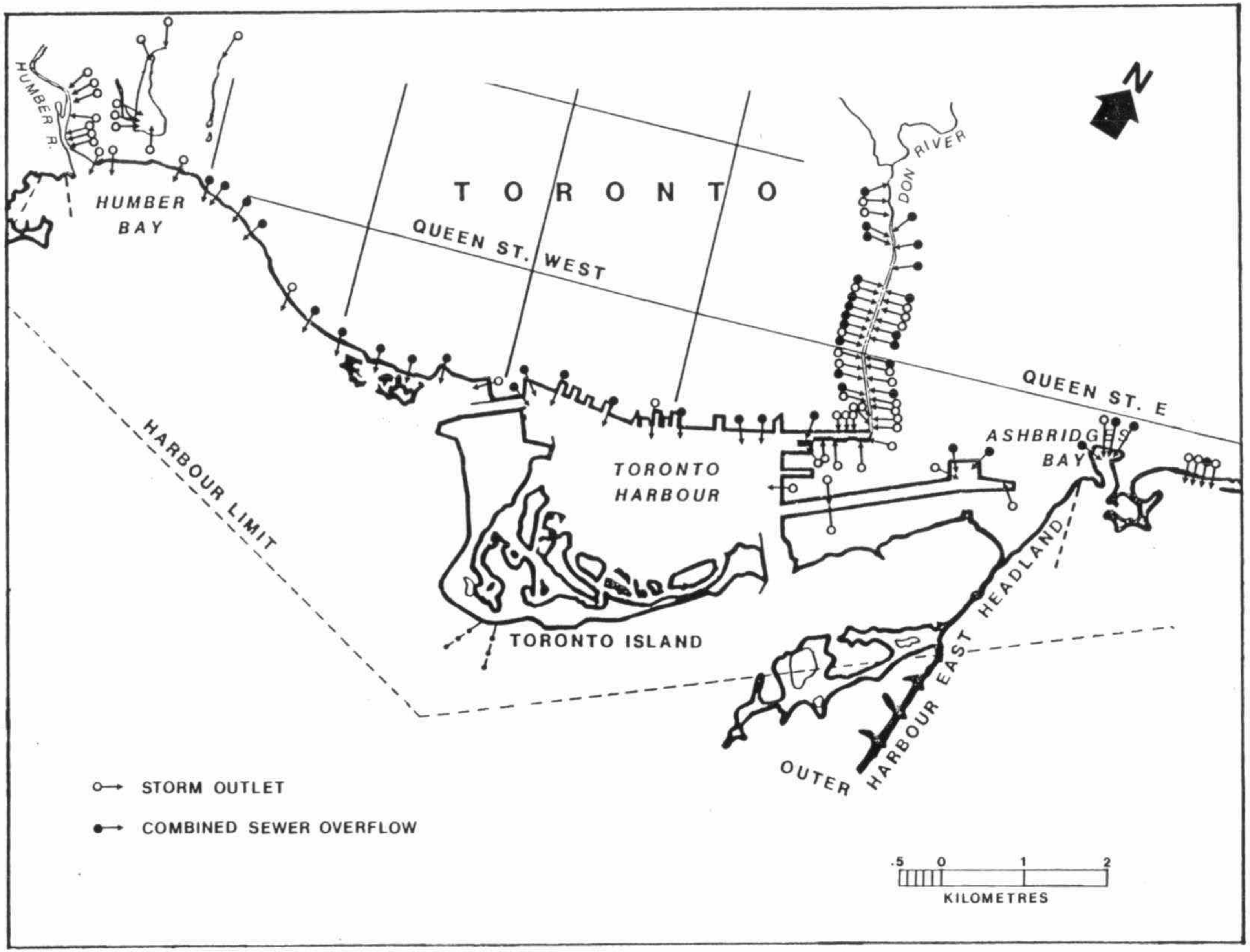

FIGURE 3.2 : MAP SHOWING STORM OUTLETS AND COMBINED SEWER OVERFLOWS INTO LAKE ONTARIO AND OPEN WATER COURSES

Table 3.21: Concentrations of Metal in Sediment(p.p.m.,dry weight) and in Benthic Tissue(p.p.m.,dry weight gut corrected) - Copper, Zinc, Lead, Cadmium

Location	Station	Copper			Zinc			Lead			Cadmium		
		Sediment	Benthic Tissue	BCF	Sediment	Benthic Tissue	BCF	Sediment	Benthic Tissue	BCF	Sediment	Benthic Tissue	BCF
Windermere Basin	2089	272.2	29.1	0.1	2216.4	142.2	0.1	368.0	-4.2‡	0.0	14.9	0.2	0.0
	2090	249.7	43.2	0.2	1956.7	207.4	0.1	194.8	1.3	0.0	14.0	0.3	0.0
Outside Ham. Harb.	2097	23.7	44.5	1.9	146.2	547.2	3.7	60.0	-0.5‡	0.0	2.7	0.2	0.1
Humber Bay	2113	161.6	22.5	0.1	350.9	125.0	0.4	287.8	6.8	0.0	6.8	0.2	0.0
	2115	427.6	19.9	0.0	1737.6	71.8	0.0	311.5	0.3	0.0	57.3	-0.2‡	0.0
	2118	161.5	48.8	0.3	442.0	227.8	0.5	244.4	8.5	0.0	12.6	1.1	0.1
	2330	28.2	34.2	1.2	566.5	147.8	0.3	206.3	0.0	0.0	11.4	0.2	0.0
	2331	113.8	24.6	0.2	578.5	144.7	0.3	224.1	-0.3‡	0.0	13.3	0.2	0.0
	2334	46.1	21.8	0.5	145.2	154.1	1.1	88.1	0.7	0.0	3.9	0.3	0.1
	2335	54.3	82.0	1.5	334.1	408.8	1.2	174.9	0.1	0.0	8.1	0.2	0.0
	2369	67.6	21.2	0.3	496.9	97.5	0.2	241.4	-1.8‡	0.0	9.2	0.2	0.0
	2370	332.1	19.6	0.1	1354.8	91.9	0.1	245.2	0.4	0.0	47.1	-0.2‡	0.0
	2371	121.5	20.7	0.2	531.7	189.8	0.4	249.5	9.9	0.0	10.9	0.2	0.0
Toronto Harbour	1346	60.1	24.4	0.4	471.5	195.0	0.4	460.3	-6.0‡	0.0	9.2	0.2	0.0
	1352	76.8	43.7	0.6	437.6	210.7	0.5	324.8	-1.8‡	0.0	9.1	0.2	0.0
	1354	34.1	43.1	1.3	482.5	245.3	0.5	284.0	54.6	0.2	5.7	0.1	0.0
	1357	71.4	33.7	0.5	401.4	182.4	0.5	420.0	13.1	0.0	9.4	0.2	0.0
	1362	45.4	59.5	1.3	367.5	261.0	0.7	170.2	47.5	0.3	5.4	0.2	0.0
	1365	63.4	31.0	0.5	330.4	239.0	0.7	306.9	4.2	0.0	8.0	0.2	0.0
	1366	73.5	50.0	0.7	431.9	283.0	0.7	226.1	10.4	0.0	8.2	0.2	0.0
	1371	49.7	79.1	1.6	358.3	239.7	0.7	156.3	41.5	0.3	5.7	0.2	0.0
	1379	31.1	37.4	1.2	249.7	191.8	0.8	108.3	-2.5‡	0.0	1.2	0.2	0.2
Eastern Headland	2108	48.1	54.4	1.1	99.8	663.4	6.6	116.4	12.6	0.1	2.1	1.1	0.5
	2277	87.6	77.3	0.9	257.9	458.5	1.8	242.9	20.4	0.1	4.7	0.5	0.1
	2280	56.6	70.1	1.2	143.6	463.3	3.2	164.3	28.0	0.2	2.6	1.2	0.5
	2284	108.6	55.3	0.5	333.0	325.5	1.0	307.0	26.3	0.1	4.5	0.2	0.0
	2373	53.8	30.1	0.6	97.4	285.2	2.9	107.7	36.3	0.3	1.2	0.3	0.3
Ashbridges Bay	2034	72.9	34.6	0.5	401.3	239.0	0.6	315.3	-8.7‡	0.0	3.9	0.2	0.0
E. Tor. Waterfront	2101	11.1	15.7	1.4	25.9	135.2	5.2	34.4	0.5	0.0	2.1	0.3	0.1
	2102	16.9	76.8	4.5	59.3	207.6	3.5	66.2	-0.8‡	0.0	2.6	0.2	0.1
	2103	14.6	15.6	1.1	40.3	116.4	2.9	44.8	0.2	0.0	2.1	0.3	0.1
	2082	13.4	41.0	3.1	31.1	232.7	7.5	35.8	-0.1‡	0.0	2.0	0.2	0.1
	2083	16.9	25.2	1.5	48.6	62.9	1.3	103.4	-1.4‡	0.0	2.5	0.2	0.1
St. Clair River	66	22.3	9.6	0.4	43.3	82.2	1.9	20.2	2.7	0.1	0.8	0.3	0.4
Niagara River	113	99.3	54.3	0.5	209.9	282.6	1.3	187.1	60.6	0.3	4.3	0.2	0.0
	157	77.9	15.5	0.2	97.9	165.7	1.7	158.6	-1.3‡	0.0	4.1	0.2	0.0
	160	18.6	12.9	0.7	125.9	131.1	1.0	27.1	2.5	0.1	0.9	0.3	0.3
	183	131.7	19.7	0.1	687.8	164.5	0.2	165.2	-1.5‡	0.0	5.4	0.2	0.0
St. Marys River	45	23.1	22.5	1.0	118.7	131.3	1.1	54.4	2.4	0.0	1.0	0.3	0.3
	46	166.9	24.0	0.1	730.3	115.8	0.2	217.4	0.2	0.0	3.5	0.3	0.1
	47	89.4	11.4	0.1	493.8	107.5	0.2	157.1	1.2	0.0	2.0	0.3	0.2
	48	168.1	17.0	0.1	947.3	110.7	0.1	619.3	6.8	0.0	4.5	0.3	0.1

‡ See Text For Explanation Regarding Negative Values

BCF = Bioconcentration Factors (Contaminant concentration in benthic tissue/contaminant concentration in sediment)

Table 3.21 cont'd: Concentrations of Metal in Sediment(p.p.m.,dry weight) and in Benthic Tissue(p.p.m.,dry weight gut corrected) - Iron, Manganese, Mercury

		Iron			Manganese			Mercury			Arsenic		
Location	Station	Sediment	Benthic Tissue	BCF	Sediment	Benthic Tissue	BCF	Sediment	Benthic Tissue	BCF	Sediment	Benthic Tissue	BCF
Windermere Basin	2089	6135.0	1310.3	0.2	690.3	21.8	0.0	1.0	0.1	0.1	--	--	--
	2090	5531.4	2216.8	0.4	684.4	35.3	0.1	0.8	0.1	0.2	--	--	--
Outside Ham. Harb.	2097	4104.1	4781.1	1.2	646.6	183.7	0.3	0.2	0.4	2.0	--	--	--
Humber Bay	2113	11558.4	634.1	0.1	395.7	19.9	0.1	0.4	0.2	0.5	13.3	1.3	0.1
	2115	15738.2	327.1	0.0	438.7	13.4	0.0	1.3	0.1	0.1	14.5	3.5	0.2
	2118	9935.9	1114.6	0.1	292.4	21.0	0.1	0.6	0.3	0.5	7.4	0.7	0.1
	2330	7724.4	1115.9	0.1	242.9	16.5	0.1	0.4	0.2	0.5	--	--	--
	2331	7059.0	1369.0	0.2	248.1	9.6	0.0	0.4	0.2	0.5	--	--	--
	2334	2244.4	1303.8	0.6	181.1	30.3	0.2	0.2	0.2	1.0	--	--	--
	2335	5803.1	4730.5	0.8	168.5	92.3	0.5	0.1	0.4	4.0	--	--	--
	2369	5680.7	1015.3	0.2	196.1	12.9	0.1	0.3	0.1	0.3	--	--	--
	2370	9899.0	857.2	0.1	270.9	22.6	0.1	0.8	0.2	0.3	8.3	0.7	0.1
	2371	8068.5	772.1	0.1	438.7	18.7	0.0	0.2	0.1	0.5	6.6	1.0	0.2
Toronto Harbour	1346	4716.4	1647.6	0.3	142.4	14.3	0.1	0.6	0.2	0.3	--	--	--
	1352	13114.1	2132.6	0.2	391.2	40.3	0.1	0.3	0.3	1.0	--	--	--
	1354	8238.2	2778.3	0.3	227.8	11.5	0.1	0.4	0.4	1.0	--	--	--
	1357	8872.2	41655.7	4.7	180.6	30.6	0.2	0.3	0.2	0.7	--	--	--
	1362	8431.2	5136.4	0.6	227.9	39.0	0.2	0.1	0.5	5.0	--	--	--
	1365	7678.6	2657.2	0.3	425.8	32.9	0.1	0.3	0.3	1.0	--	--	--
	1366	7600.1	2356.2	0.3	381.5	9.3	0.0	0.3	0.3	1.0	--	--	--
	1371	8065.5	3441.4	0.4	203.3	28.8	0.1	0.1	0.3	3.0	--	--	--
	1379	4576.7	720.5	0.2	217.3	1.2	0.0	0.1	0.3	3.0	--	--	--
Eastern Headland	2108	4797.7	2341.4	0.5	325.7	68.8	0.2	0.1	0.2	2.0	6.0	0.8	0.1
	2277	10334.7	1622.2	0.2	403.2	44.0	0.1	0.3	0.4	1.3	11.6	1.8	0.2
	2280	9582.5	3260.3	0.3	458.6	50.0	0.1	0.1	0.4	4.0	5.3	3.6	0.7
	2284	11647.2	1839.1	0.2	442.2	17.4	0.0	0.4	0.5	1.3	--	--	--
	2373	6818.2	394.0	0.1	491.8	14.3	0.0	0.3	0.3	1.0	--	--	--
Ashbridges Bay	2034	3921.0	6117.3	1.6	83.8	72.5	0.9	0.8	0.2	0.2	--	--	--
E. Tor. Waterfront	2101	1631.8	790.2	0.5	121.5	7.5	0.1	0.1	0.1	1.0	--	--	--
	2102	1769.3	2136.6	1.2	171.3	6.0	0.0	0.4	0.4	1.0	--	--	--
	2103	2023.3	849.5	0.4	116.2	-0.6	0.0	0.1	0.1	1.0	--	--	--
	2082	1924.0	2997.1	1.6	136.9	24.6	0.2	0.2	0.2	1.0	--	--	--
	2083	2230.8	2403.3	1.1	159.1	34.5	0.2	0.1	0.2	2.0	--	--	--
St. Clair River	66	5135.9	533.3	0.1	210.8	11.9	0.1	--	--	--	--	--	--
Niagara River	113	10725.2	9843.7	0.9	461.5	145.8	0.3	1.0	0.3	0.3	16.9	21.6	1.3
	157	8914.1	390.5	0.0	306.0	4.6	0.0	--	--	--	--	--	--
	160	3589.0	1416.8	0.4	123.1	22.4	0.2	--	--	--	--	--	--
	183	13339.0	23817.2	1.8	430.1	34.7	0.1	--	--	--	--	--	--
St. Marys River	45	6272.3	1030.2	0.2	64.9	39.6	0.6	0.1	0.5	5.0	--	--	--
	46	15043.8	258.2	0.0	197.1	12.0	0.1	0.6	0.3	0.5	34.3	18.0	0.5
	47	8949.2	715.1	0.1	128.0	8.5	0.1	0.4	0.1	0.3	--	--	--
	48	13280.3	104.2	0.0	362.4	-1.2‡	0.0	0.6	0.0	0.0	--	--	--

-- No Data Available

‡ See Text For Explanation Regarding Negative Values

BCF = Bioconcentration Factors (Contaminant concentration in benthic tissue/contaminant concentration in sediment)

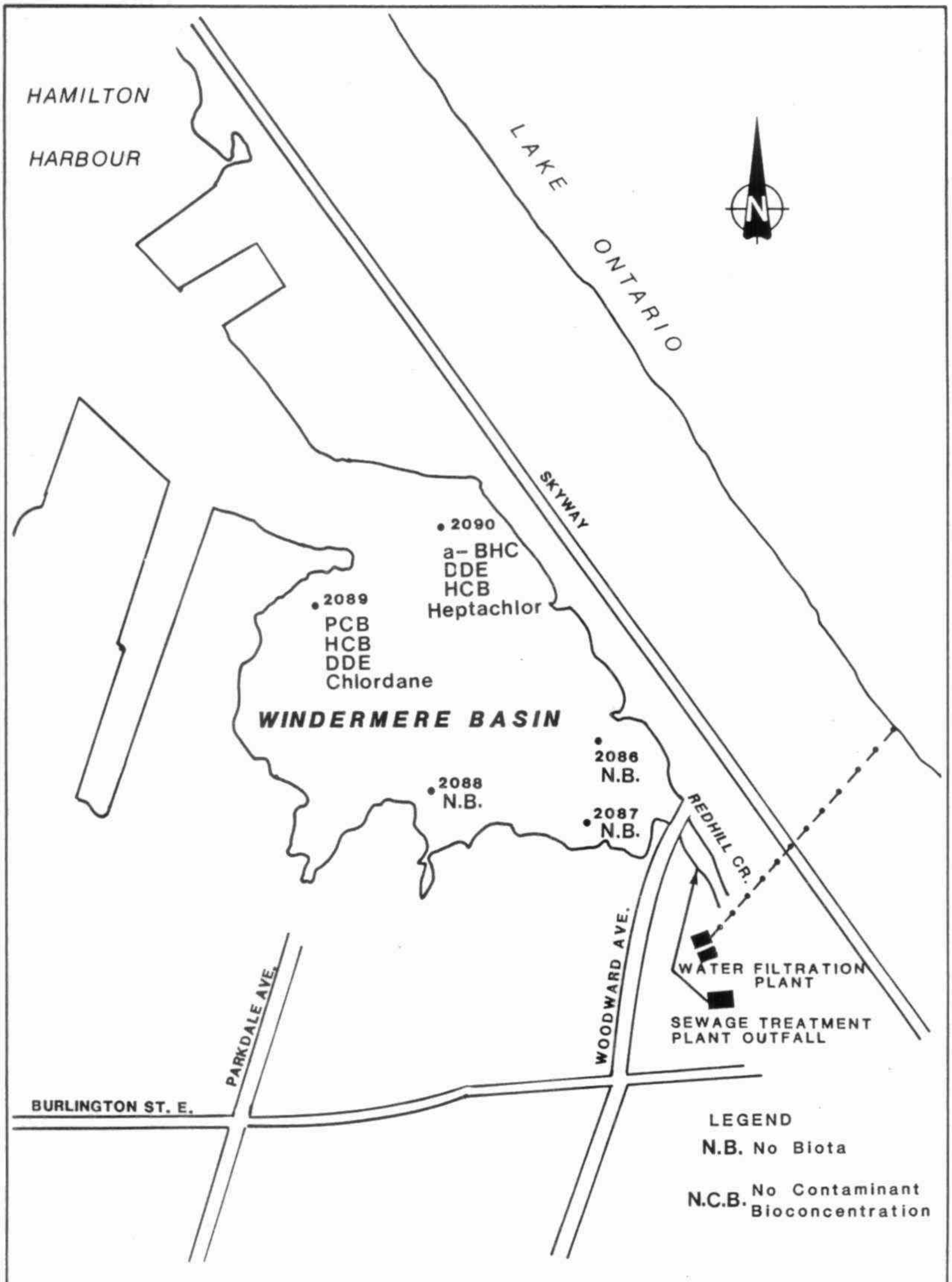

FIGURE 3.3a : WINDERMERE BASIN- STATION LOCATIONS AND PARAMETERS SHOWING BIOCONCENTRATION FACTOR ≥ 1

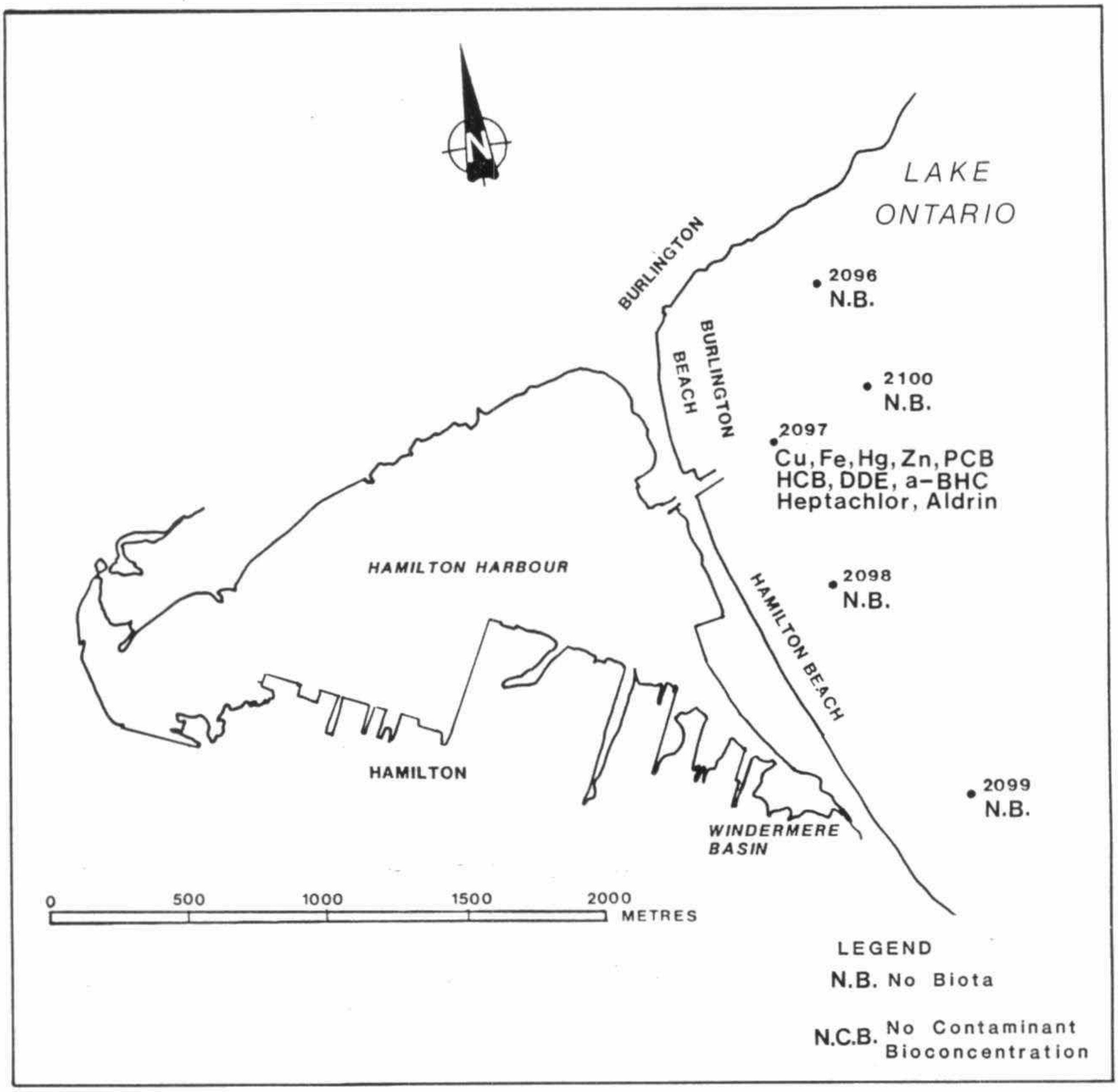

FIGURE 3.3b : OUTSIDE HAMILTON HARBOUR– STATION LOCATIONS AND PARAMETERS SHOWING BIOCONCENTRATION FACTOR ≥ 1

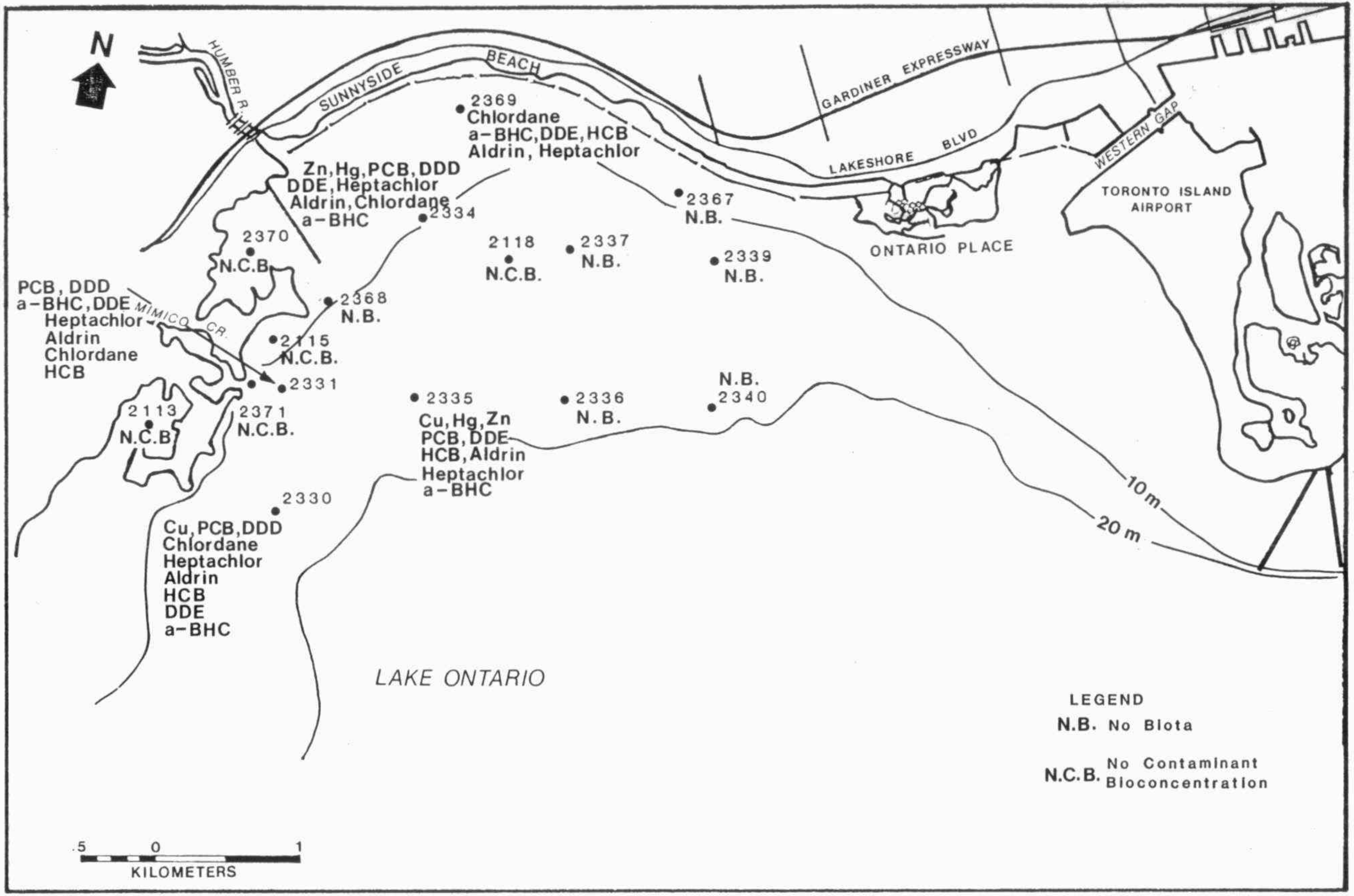

FIGURE 3.3c: HUMBER BAY- STATION LOCATIONS AND PARAMETERS SHOWING BIOCONCENTRATION FACTOR ≥ 1

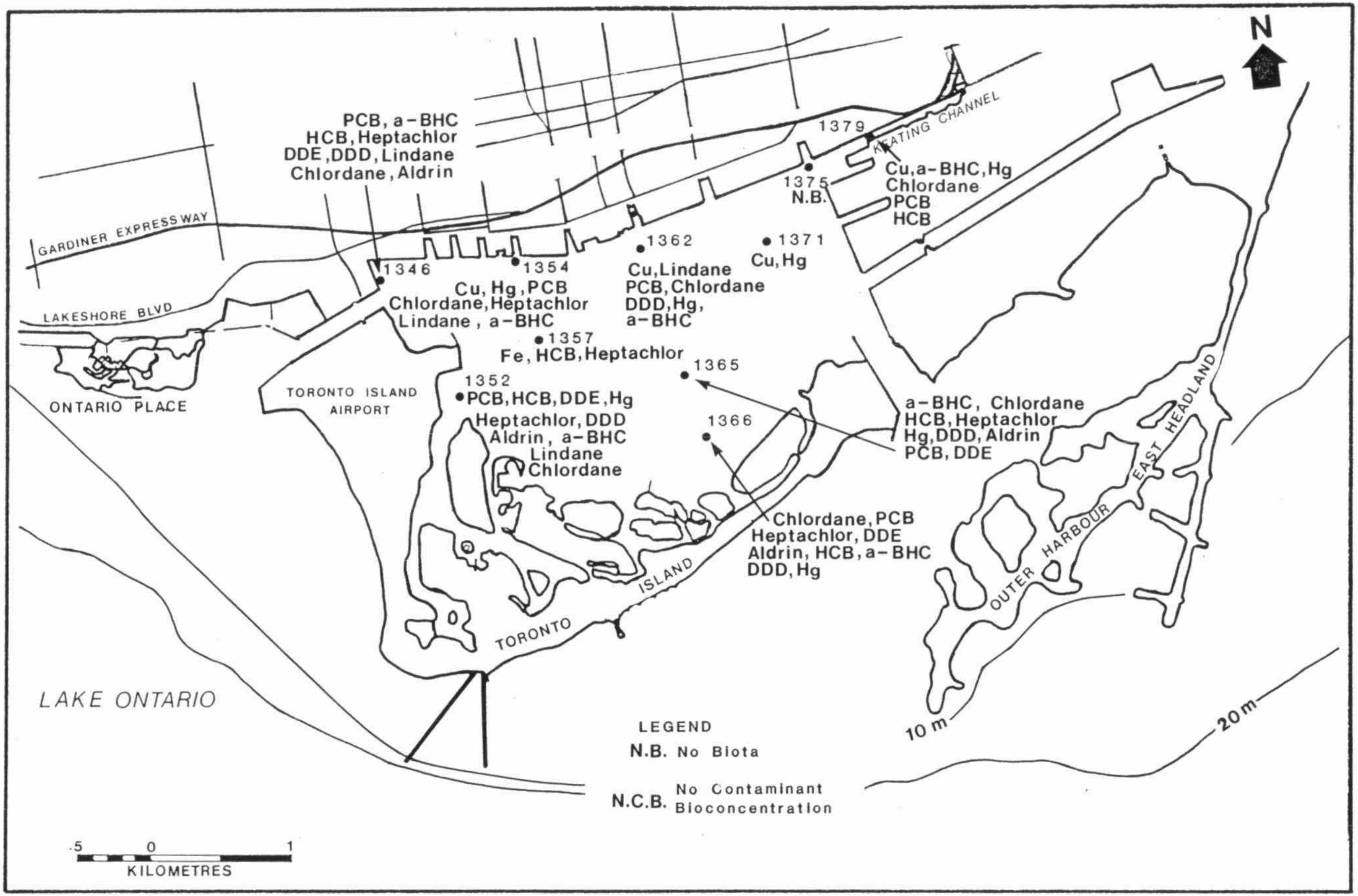

FIGURE 3.3d : TORONTO HARBOUR - STATION LOCATIONS AND PARAMETERS SHOWING BIOCONCENTRATION FACTOR ≥ 1

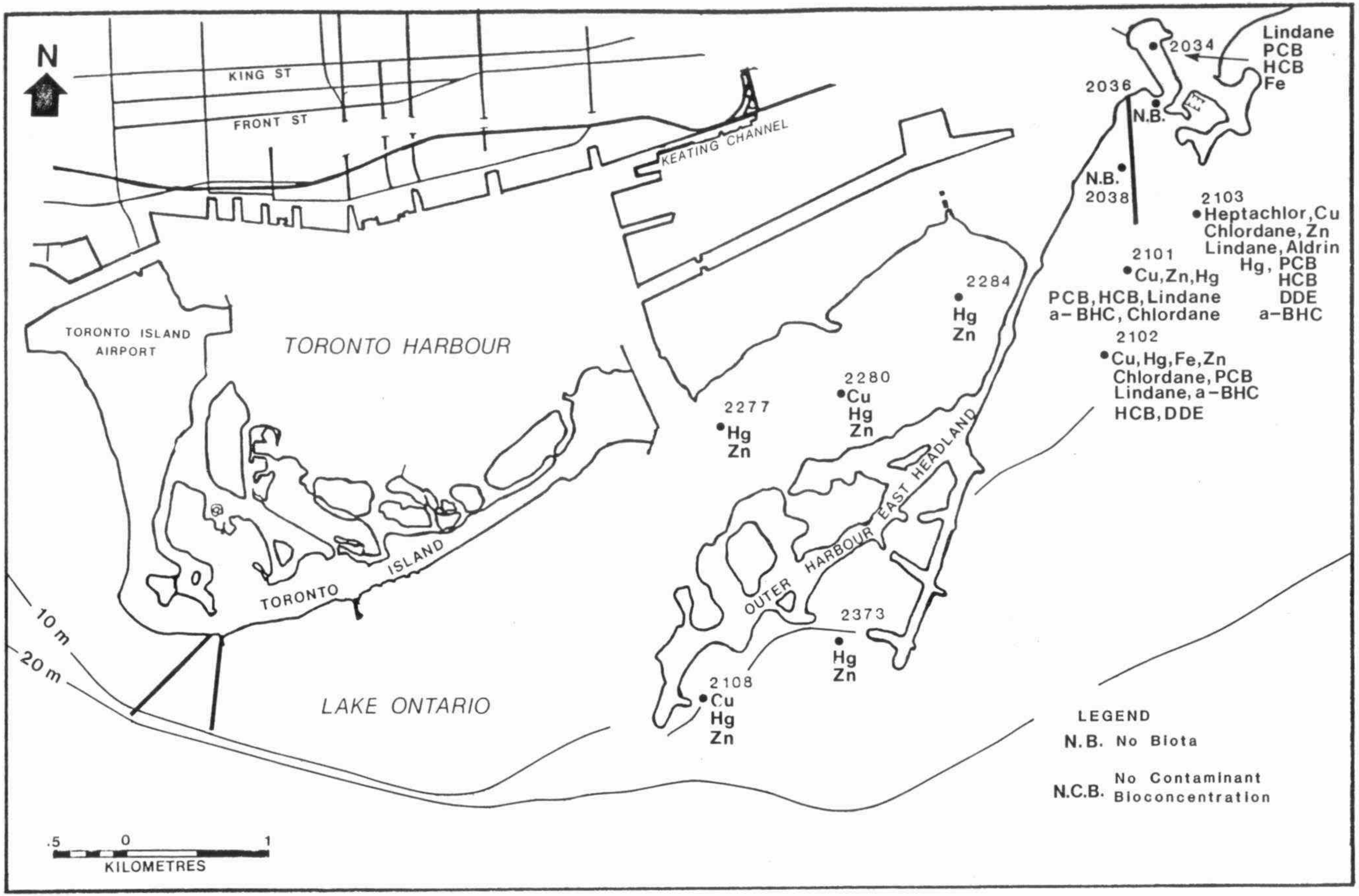

FIGURE 3.3e : EASTERN HEADLAND AND ASHBRIDGES BAY- STATION LOCATIONS AND PARAMETERS SHOWING BIOCONCENTRATION FACTOR ≥1

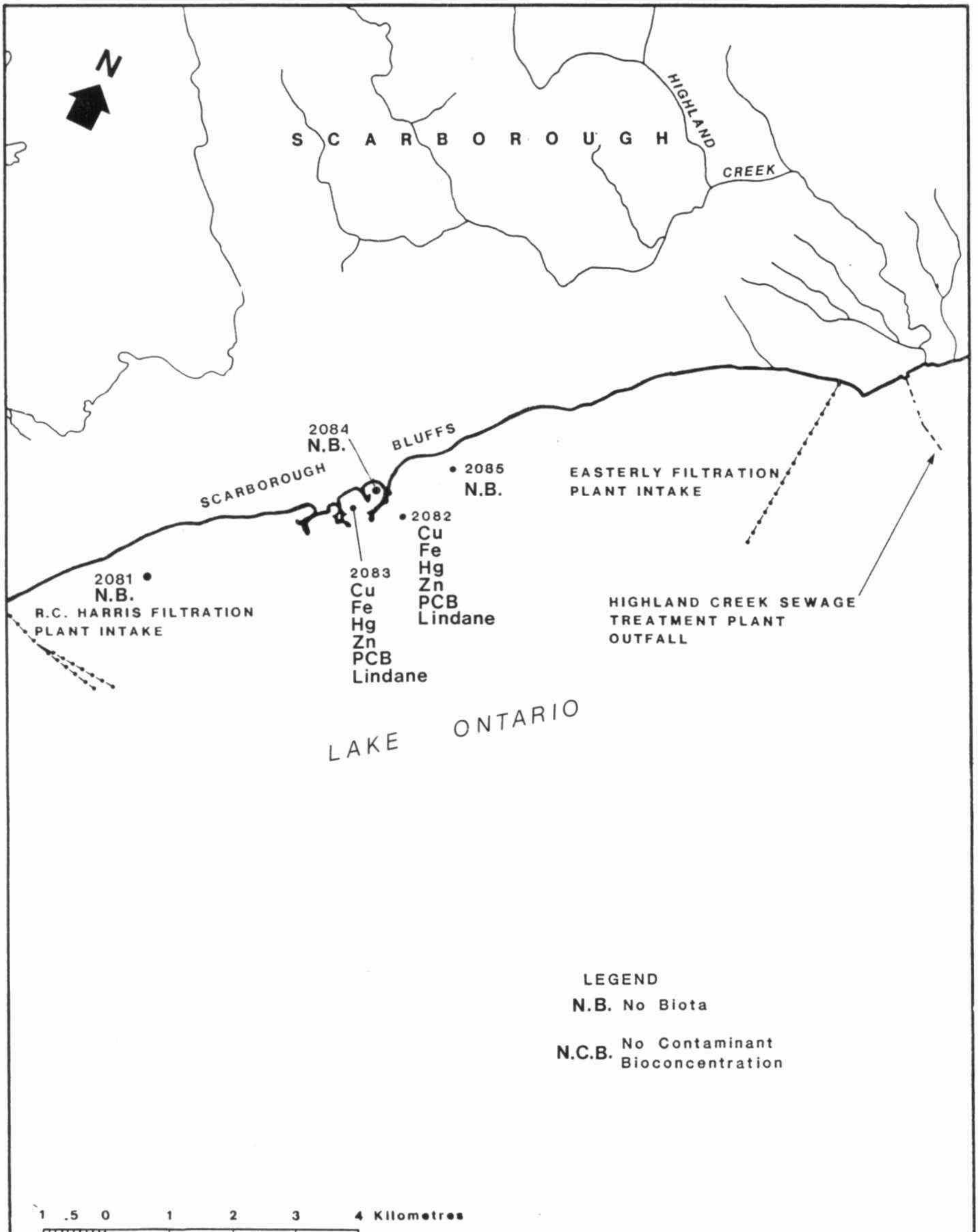

FIGURE 3.3f : SCARBOROUGH BLUFFS- STATION LOCATIONS AND PARAMETERS SHOWING BIOCONCENTRATION FACTOR ≥1

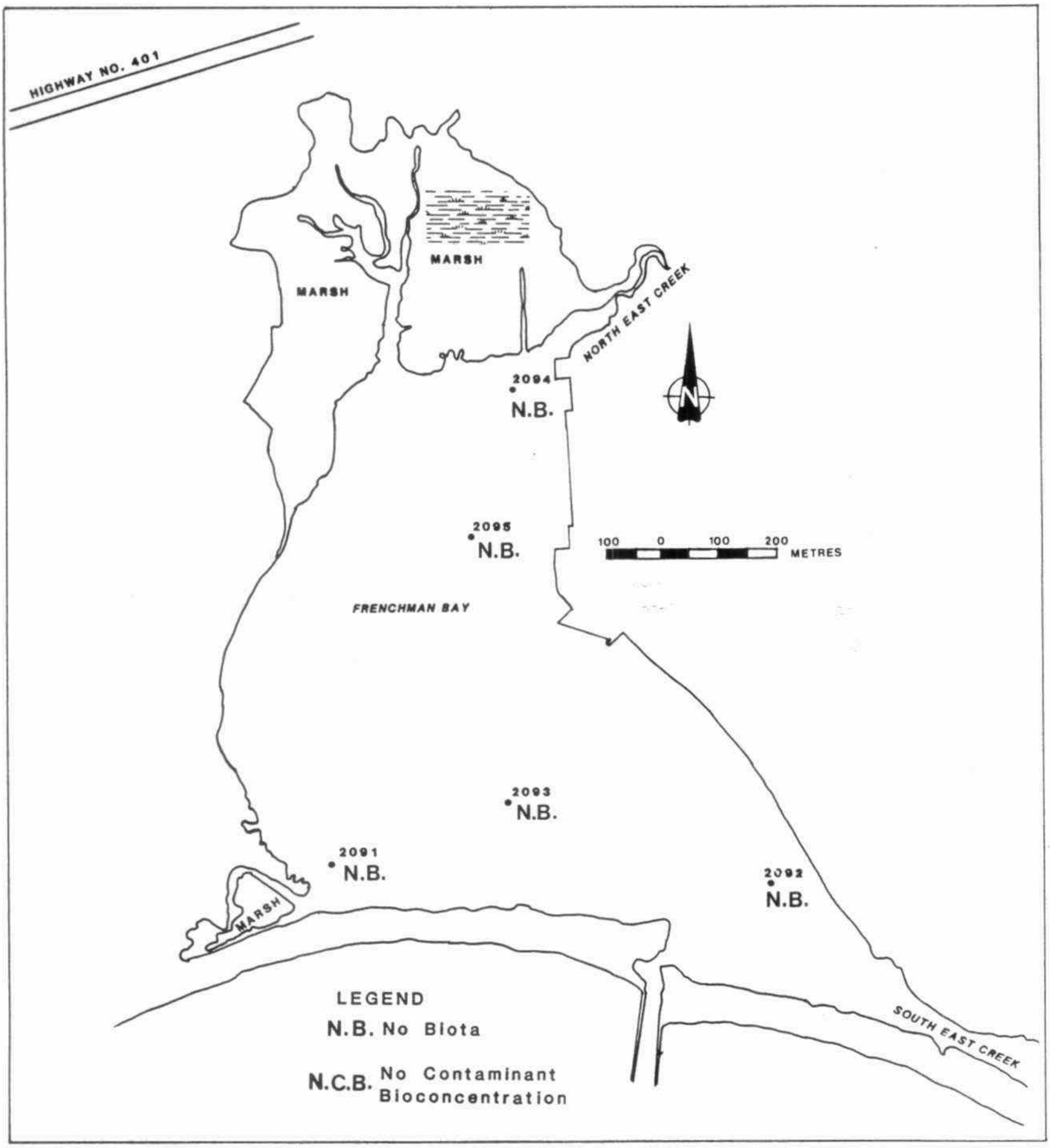

FIGURE 3.3g : FRENCHMAN BAY- STATION LOCATIONS AND PARAMETERS SHOWING BIOCONCENTRATION FACTOR ≥ 1

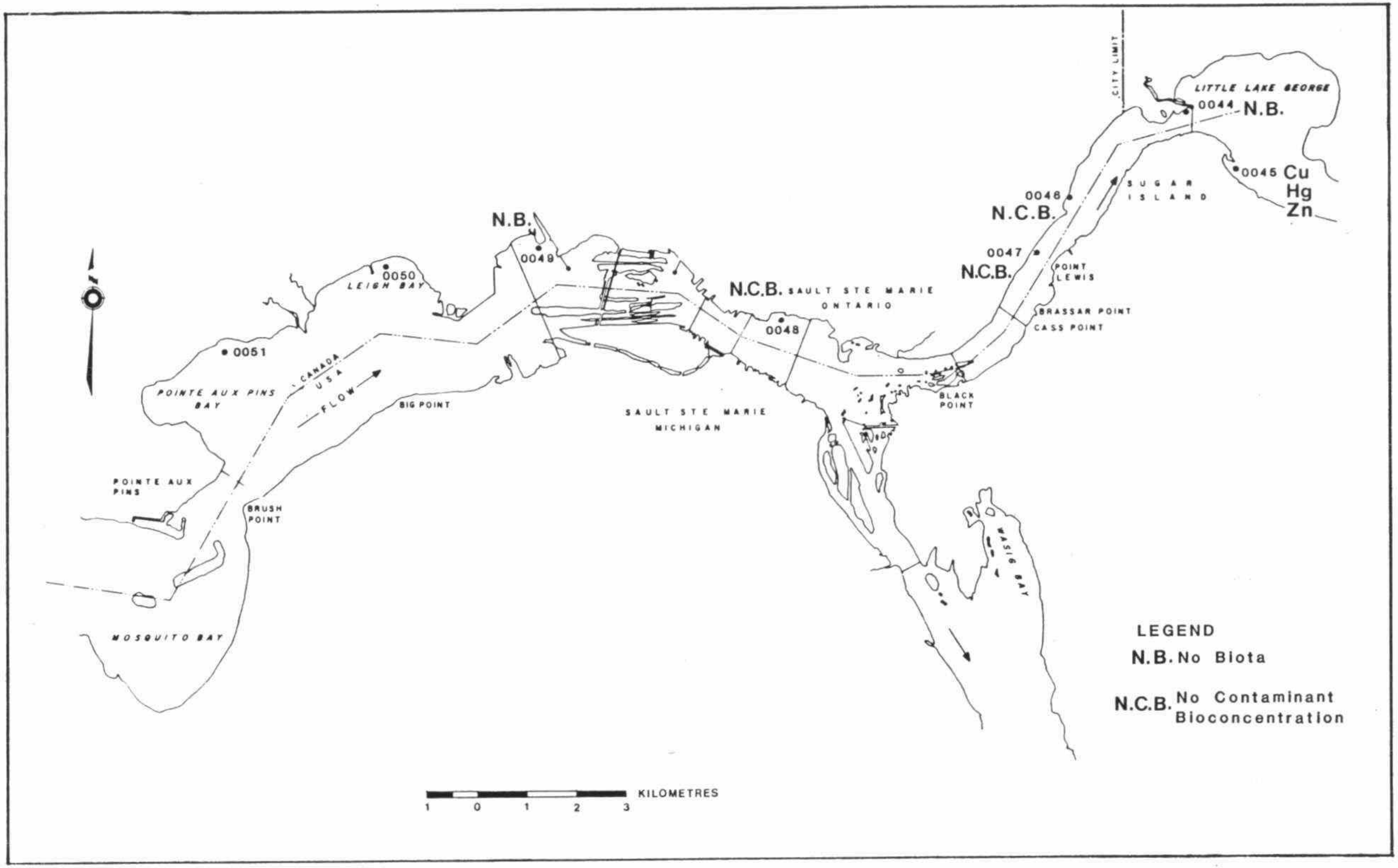

FIGURE 3.3h : ST. MARYS RIVER– STATION LOCATIONS AND PARAMETERS SHOWING BIOCONCENTRATION FACTOR ≥ 1

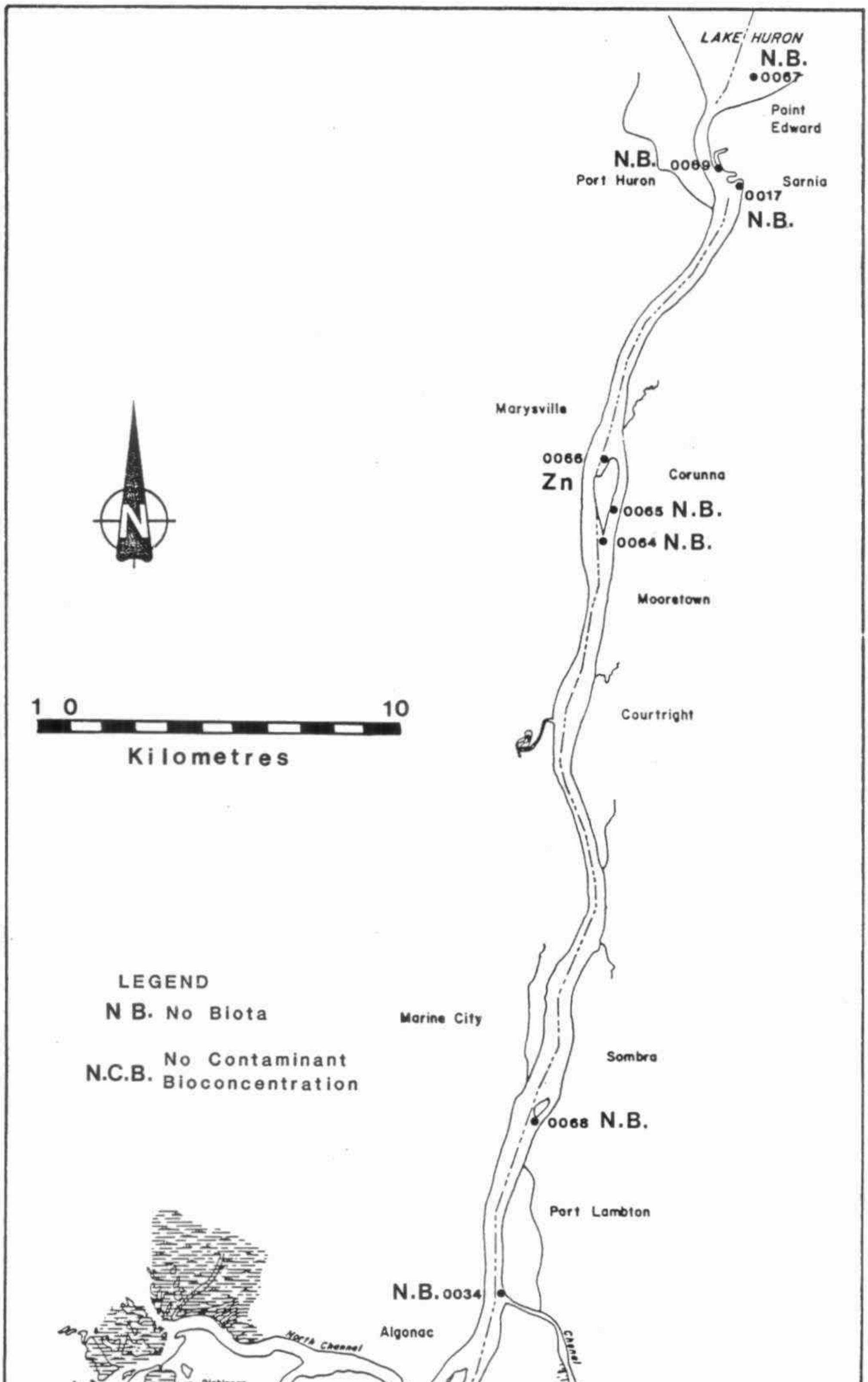

FIGURE 3.3i : ST. CLAIR RIVER– STATION LOCATIONS AND PARAMETERS SHOWING BIOCONCENTRATION FACTOR ≥1

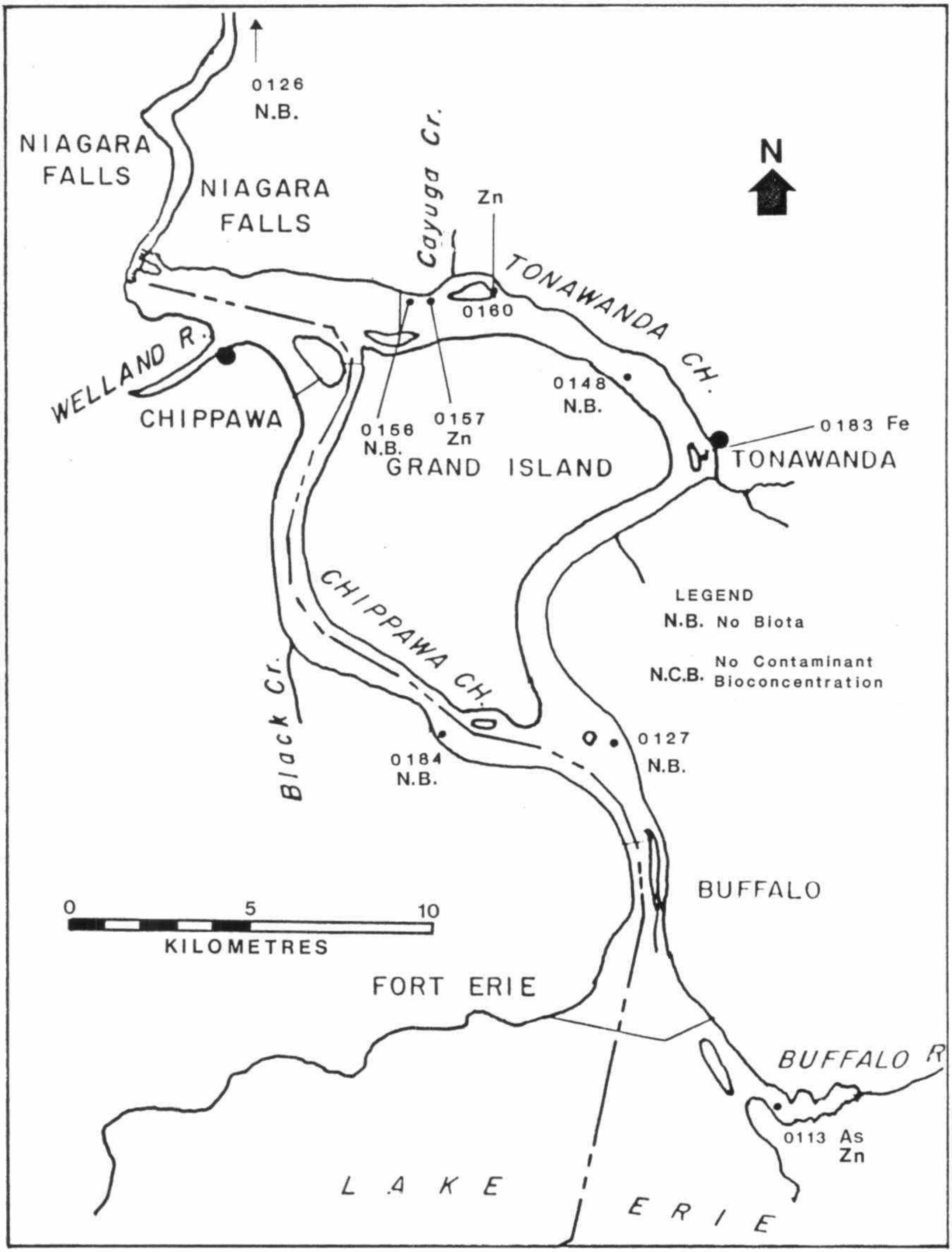

FIGURE 3.3j : NIAGARA RIVER- STATION LOCATIONS AND PARAMETERS SHOWING BIOCONCENTRATION FACTOR ≥ 1

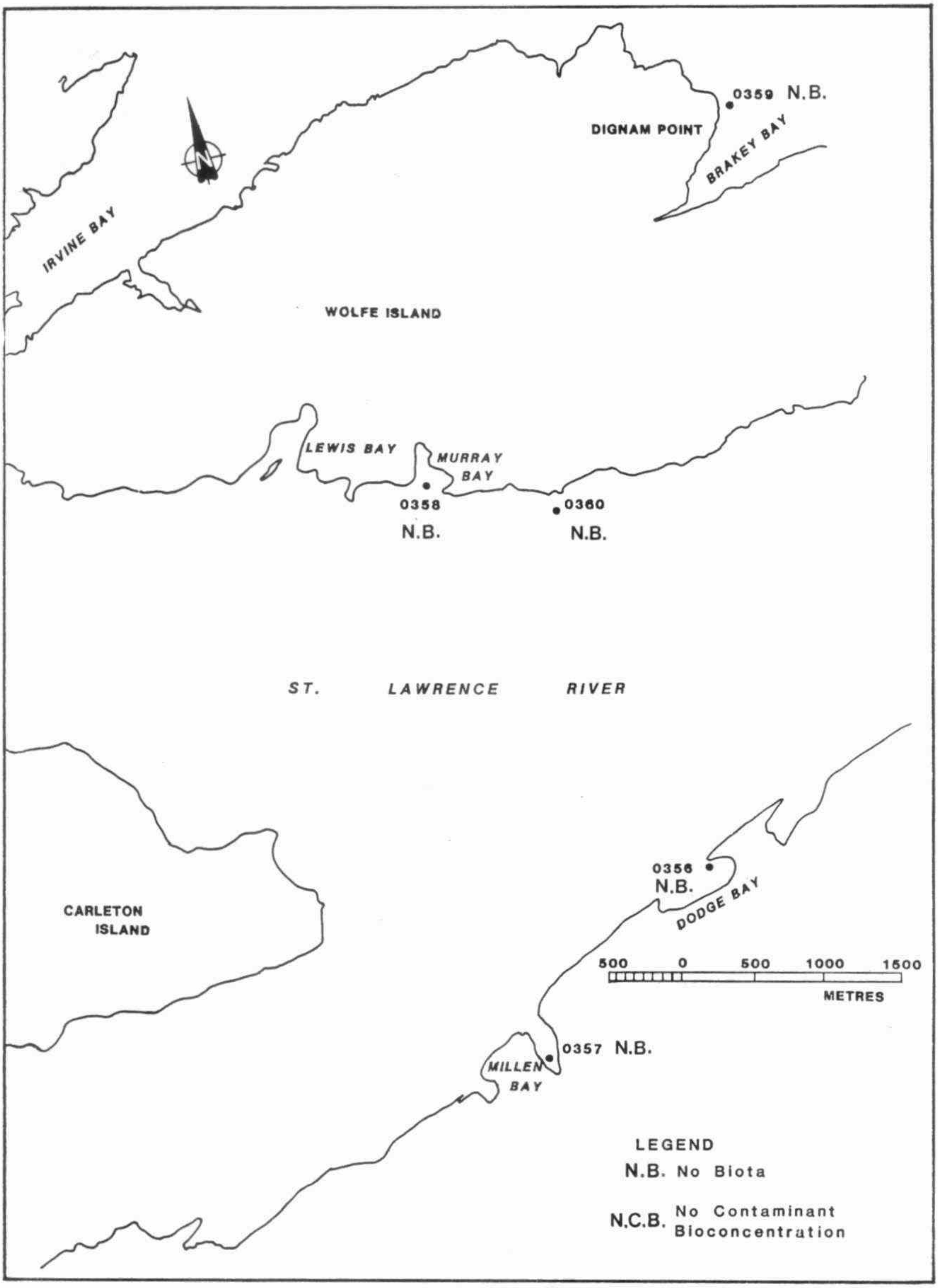

FIGURE 3.3k : ST. LAWRENCE RIVER– STATION LOCATIONS AND PARAMETERS SHOWING BIOCONCENTRATION FACTOR ≥1

showing body burden values of well over 100 ppm. The tissue concentrations were lower than iron but much higher than those of the other metals.

The body burden values of iron were generally lower than those of sediment, however, at 7 of the 42 stations, concentration factors of one or greater were noted. Most of these stations were located on the Toronto waterfront.

Mercury (Hg) in biota ranged from 0.07 ppm to 0.52 ppm and there appeared to be an upper limit to which mercury was concentrated in oligochaetes. Most of the values in organisms fell within the range of 0.2 to 0.5 ppm. Although the highest mercury concentrations in sediment were noted in the Niagara River, the organisms from this river showed very low uptake compared to most Toronto area stations.

3.3.2 Relationship Of Zinc And Copper In Biota To The Geochemical Phases Of Sediment.

The bioconcentration factors in Table 3.21 show 18 of the 42 stations for zinc and 15 of the 42 stations for copper with Zn and Cu levels in biota higher than those of the sediment. Among these, there were 10 common stations. Most of these stations were around the East Headland/Toronto Main STP. Four stations in Toronto Harbour showed Cu bioconcentration factors greater than one. Zinc values in biota were not elevated above sediment values in the harbour.

In general, with the exception of Hg, copper is the only metal that showed bioconcentration factors ≥ 1 in Toronto Harbour and this was limited to only the four stations referred to above. Most stations around the East Headland showed accumulation of Cu, Zn, and Hg by biota.

Forward stepwise regression analyses were carried out on the Zn and Cu sediment data from the respective stations with bioconcentration factors ≥ 1 in an attempt to identify parameters that may have an influence on body burden levels of these metals. The results are summarized in Table 3.22.

Table 3.22 RESULTS OF FORWARD STEPWISE*

REGRESSION ANALYSIS

Where Bioconcentration Factors ≥ 1 (Cu N = 16, Zn N = 17)
Dependent Variable :
Log Body Burden(dry weight, gut corrected concentrations in benthic tissue)

Zinc			Copper		
Independent Variables	Partial R^2	Probability	Independent Variables	Partial R^2	Probability
LOG F4(Zn)	0.47	≤ 0.01	LOG F3(Cu)	0.67	≤ 0.01
LOG LOI	0.43	< 0.02	EH	0.21	< 0.09
LOG SILT	0.28	< 0.06	LOG F1(Cu)	0.17	< 0.14
LOG F2(Zn)	0.17	< 0.16			
LOGMN	0.12	< 0.24			
ADJUSTED R SQUARED = 0.57			ADJUSTED R SQUARED = 0.61		
R SQUARED = 0.70			R SQUARED = 0.69		
MULTIPLE R = 0.84			MULTIPLE R = 0.83		

Zinc levels in biota appeared to be strongly related to the F4 phase of sediment (moderately reducible Fe/Mn oxyhydroxides) while Cu levels in biota showed a strong relationship to the F3 phase (organic/sulphide fraction) phase of sediment. Zinc levels in biota also showed a negative correlation with loss on ignition suggesting that Zn associated with organic matter may not be bioavailable.

4.0 DISCUSSION

4.1 Sediment Data

Contaminant levels in sediment showed considerable variation within and among the various study locations. High values for most parameters were noted in areas with industrial/municipal discharges such as Windermere Basin, Hamilton Harbour, Toronto Harbour, Humber Bay and St. Marys River. Among the Lake Ontario locations studied, Windermere Basin was the most contaminated area followed by Toronto Harbour and Humber Bay. The cleanest sediments were found along the Eastern Toronto Waterfront and at stations outside Hamilton Harbour. Among the rivers, St. Marys River had the highest levels of metals (except Hg) and solvent extractables which is perhaps due mainly to the large steel manufacturing industry discharging to the river. The sediments from the other rivers were much cleaner, approximating those of the Eastern Toronto Waterfront in quality. High levels of chromium were noted in Windermere Basin, Humber Bay and Toronto Harbour and is perhaps a reflection of high usage of this metal within large urban areas. The highest levels of mercury were noted in St. Clair and Niagara Rivers.

There were some distinctive variations in certain parameters among the areas sampled. Windermere Basin and Frenchman Bay showed high degree of organic enrichment. In Windermere Basin, this enrichment appears to be due mainly to solvent extractable type materials (oils and greases) whereas in Frenchman Bay, the sediments contain significant quantities of peat.

Organic pesticides were measured at very low concentrations in sediments and in many instances were below analytical detection limits.

Most chemical contaminants were associated with the fine-grained sediment (silt and clay particles). Strong correlations were noted between bulk chemical parameters in sediment and the organic content of the sediment, suggesting that the distribution pattern of the parameters is governed mainly by their association with organic material especially the solvent extractables (oils and greases). The strong relationship between metals and the organic content of sediments was supported by

findings from sequential extraction data which showed that the largest fraction of most metals (except Fe and Mn) was contained in the F3 phase (organic/sulphide). Iron was concentrated mainly in the residual phase and manganese was divided equally between the F3 and residual phases.

With the exception of Fe and to some extent Mn, most metals were in geochemically available forms (i.e. non-residual forms), which also suggested that a large fraction of the metals originated from anthropogenic sources.

The Fe and Mn oxyhydroxide fractions (F2 and F4) which have been reported in the literature (Forstner and Whittman, 1981) as important "carrier particles" of other metals, played very minor roles in comparison with the organic particles. The highest values of metals in the residual phase were noted consistently for sediments from the Eastern Toronto Waterfront. This area is exposed to the influence of waves and currents which minimize the deposition of fine-grained sediment. As a result, the substrate consists mainly of sandy material in which a significant proportion of the metals are inertly bound.

Based on the high degree of intercorrelation between parameters at the Toronto East Headland and in the St. Marys River, it appears that in addition to parameter association with fine-grained sediment, contaminant distribution is influenced by common sources in these respective areas. In the other areas sampled, the inter-relationships between parameters appear to be due mainly to their common association with organic "carrier particles" in sediment.

4.2 Biological Data

One of the basic assumptions in the design of the In-Place Pollutants Program was that there is a relationship between the levels of contaminants in benthic organisms and those of sediment since these organisms live in and process sediment for food. The two routes by which contaminants can be transferred from the environment to benthic tissue are through absorption from solution and from food sources (ie. transfer via the digestive process). The accumulation of metals in the

digestive glands of certain benthic organisms has been documented (Elder and Mattraw 1984, Newman and McIntosh, 1983) suggesting uptake via food sources and laboratory studies have demonstrated that benthic organisms can take up significant levels of PCB's directly from sediment (Meier and Rediske, 1984, Fowler et al., 1978). The study by Fowler, et al. examined the contribution of both water and sediment to PCB uptake by benthic worms and found that although uptake of PCB's from water was very rapid compared to uptake from sediment, the water route was of little importance because of the generally low levels of PCB in water compared to sediment concentrations. The study concluded that sediment was the more important of these two routes of uptake. The literature also reports several studies which showed significant uptake of contaminants from water by benthic organisms (Sanders and Chandler. 1972, Sodergren and Svenson, 1973, Marcelle and Thorme, 1984).

One of the important points that emerges from the literature is that when water contains appreciable concentrations of contaminants, especially the organochlorine contaminants (PCB/pesticides), it can represent the most significant source of contaminants to aquatic biota. With regards to benthic organisms under normal environmental conditions however, the importance of the water route is diminished because of the generally low levels at which organics such as PCBs are found in water compared with sediment (Fowler et. al., 1978).

Because of their wide geographic distribution and high population densities in Great Lakes sediments, most oligochaete studies have been centered on the Tubificid members especially T. tubifex and Limnodrilus spp. These organisms feed primarily on the top 2 to 8 cm of sediment, although they have been occasionally found at depths of 20 cm or more in sediment (McCall and Tevesz, 1982). The organisms feed with their heads down in the sediment and their posterior end exposed to the water immediately overlying the sediment (McCall and Tevesz, 1982). Respiration takes place predominantly (up to 90% in some cases - Brinkhurst and Jamieson, 1971) through the exposed tail region. This suggests that most contaminant uptake from solution will occur through the tail region and from the water column above the sediment - water interface as opposed to uptake from the interstitial water within the sediment matrix.

Tubificids feed selectively on the fine particles of sediment (silt and clays) and attached microflora such as bacteria (McCall and Tevesz, 1982). They pass large quantities of sediment through the gut and it is expected that some of the contaminants associated with the sediment will be absorbed by the organisms during digestion.

Information from the Phase 1 In-Place Pollutants study suggests that uptake from both sediment and bottom water may be important with regards to pesticides uptake by oligochaetes. At most of the stations sampled, the levels of pesticides in bottom sediments were extremely low but detectable levels were noted in the organisms at certain stations. Most of these stations were in the vicinity of discharge sources such as storm sewers and sewage treatment plant outfalls. A recent study (D. Boyd, 1987) investigated the levels of contaminants in suspended sediment at river mouths and in the final effluent at two sewage treatment plants in Toronto and found detectable levels of several pesticides in the suspended material. It appears that urban discharges represent sources of pesticides which are readily taken up by benthic organisms influenced by these discharges.

The organisms feeding on the upper sediment layers in the vicinity of these discharges may also take up contaminants from the aqueous phase during respiration since a proportion of recently discharged contaminants is likely to be present in the aqueous phase.

Once organic contaminants are in contact with sediment, the less persistent organics which include many of the organochlorine pesticides are readily degraded under anaerobic conditions (Muir and Yarechewski, 1984). The more persistent compounds such as PCBs are likely to become bound to organic matter or be dissolved in the solvent extractable fraction, which may render the contaminants unavailable. Laboratory studies have demonstrated that solvent extractables can significantly reduce the uptake of PCB's from sediments by benthic organisms (Meier and Rediske, 1984). Benthic organisms in contaminated sediments with high concentrations of solvent extractables and organic matter such as chitin and lignin (which are not easily degraded) are therefore, expected to show low levels of persistent organics such as PCBs. The data from the Phase 1 study showed that the oligochaetes obtained from

sediment with high organic content (measured as solvent extractables, loss on ignition and total organic carbon) generally had lower body burdens of Cu, Zn, Hg and PCBs compared with organisms from sediment with lower organic content (Table 4.1a-d) even though the concentrations of contaminants in the highly organic sediments were much greater. For Cu and Zn, sediments from stations with concentration factors less than one were more heavily contaminated with these metals compared to stations where concentration factors were one or greater. The data also showed very low uptake of Cd and Pb by benthic organisms. The literature suggests that Cd is not readily available to organisms under reducing conditions (Luoma, 1983). This may be one of the reasons for low Cd uptake, since most of the sediments sampled were anaerobic. Reasons for the low uptake of Pb are not readily apparent.

Information from the Phase 1 studies suggests that the tubificid members of the oligochaete can survive in sediments with relatively high levels of contamination. Other studies have shown that while tubificid worms, in particular T. tubifex and Limnodrilus spp. are tolerant of organic enrichment and anoxic sediment conditions that often accompany enrichment, these organisms are particularly intolerant of many chemical pollutants especially metals (Chapman et. al., 1982).

Findings similar to the Phase 1 In-Place Pollutants results were noted in a metal impacted lake in Indiana (Wentsel and McIntosh, 1977). The investigators in that study could not determine the mechanisms enabling the organisms to survive in sediments that were heavily contaminated with metals. Other studies (Bryan, 1975 and 1979) have shown that some species of benthic organisms can develop the capacity to survive under high metal pollution by previous exposure to sublethal levels. The tolerance developed through exposure to sublethal levels enabled the organisms to survive levels of pollution that would have been otherwise toxic. Laboratory studies have also shown that organisms from unpolluted areas that were not tolerant to Pb contamination could be made tolerant by exposure to sublethal levels of lead (Fraser, 1980). Fraser suggested that natural tolerance may be achieved by acclimation.

The ability of oligochaetes to survive in contaminated sediments and accumulate levels of various contaminants in their tissue raises concerns regarding the biological magnification of these chemicals in organisms that feed on the oligochaetes. This subject will be examined in another phase of the In-Place Pollutants Study.

** COPPER **

Table 4.1a Summary Statistics For The Distribution Of Copper In Sediment And Benthic Tissue And The Organic Content Of Sediment According To Concentration Factors (all values in ug/g dry wt. unless stated otherwise)

	Concentration Factors < 1 Median (N)	Concentration Factors < 1 Range	Concentration Factors ≥ 1 Median (N)	Concentration Factors ≥ 1 Range
Copper In Sediment				
F3 Geochemical Fraction	83.11 (27)	(17.81-399.77)	18.99 (15)	(4.93-52.56)
Total Non-Residual (Σ IW-F4)	89.37 (27)	(18.63-427.64)	28.20 (15)	(11.12-56.60)
Copper In Biota				
Benthic Organisms	24.36 (27)	(9.60-77.30)	43.09 (15)	(15.60-82.00)
Organic Content In Sediment				
TOC (mg/g)	30.0 (11)	(12.0-68.0)	12.0 (11)	(0.1-37.0)
% LOI	7.0 (15)	(1.3-17.0)	3.3 (15)	(0.3-9.4)
Oil & Grease	4125.0 (15)	(920-24410)	1360.0 (15)	(360-9270)

(N) = Number of Stations

** ZINC **

Table 4.1b Summary Statistics For The Distribution Of Zinc In Sediment And Benthic Tissue And The Organic Content Of Sediment According To Concentration Factors (all values in ug/g dry wt. unless stated otherwise)

	Concentration Factors < 1 Median (N)	Range	Concentration Factors ≥ 1 Median (N)	Range
Zinc In Sediment				
F4 Geochemical Fraction	26.04 (24)	(3.15-885.81)	10.91 (18)	(0.16-64.83)
Total Non-Residual (IW-F4)	488.11 (24)	(249.66-2216.43)	109.25 (18)	(25.89-334.07)
Zinc In Biota				
Benthic Organisms	186.10 (24)	(71.80-283.00)	220.13 (18)	(62.90-663.40)
Organic Content In Sediment				
TOC (mg/g)	30.0 (15)	(12.0-68.0)	7.0 (7)	(0.1-22.0)
% LOI	7.8 (24)	(3.2-17.0)	2.1 (17)	(0.3-8.4)
Oil & Grease	5625.0 (24)	(1140.0-24410.0)	1230.0 (17)	(360.0-3550.0)

(N) = Number of Stations

** MERCURY **

Table 4.1c Summary Statistics For The Distribution Of Mercury In Sediment And Benthic Tissue And The Organic Content Of Sediment According To Concentration Factors (all values in ug/g dry wt. unless stated otherwise)

	Concentration Factors < 1 Median (N)	Concentration Factors < 1 Range	Concentration Factors ≥ 1 Median (N)	Concentration Factors ≥ 1 Range
Hg in Sediment	0.60 (17)	(0.2-1.3)	0.16 (21)	(0.1-0.4)
Hg in Benthos	0.18 (17)	(0.1-0.3)	0.33 (21)	(0.1-0.5)
Organic Content in Sediment				
TOC mg/g	34.0 (8)	(12.0-68.0)	23.0 (14)	(0.1-37.0)
% LOI	7.0 (16)	(3.3-17.0)	3.7 (21)	(0.3-11.0)
Oil & Grease	6120.0 (16)	(1140.0-24410.0)	2150.0 (21)	(360.0-9270.0)

(N) = Number of Stations

** PCB **

Table 4.1d Summary Statistics For The Distribution Of PCB In Sediment And Benthic Tissue And The Organic Content Of Sediment According To Concentration Factors (all values in ug/g dry wt. unless stated otherwise)

	Concentration Factors < 10		Concentration Factors $\geq$ 10	
	Median (N)	Range	Median (N)	Range
PCB in Sediment	0.30 (12)	(0.03-3.09)	0.01 (10)	(0.01-0.12)
PCB in Benthos	1.24 (12)	(0.12-1.64)	1.34 (10)	(0.13-1.97)
Organic Content in Sediment				
TOC mg/g	31.0 (13)	(12.0-53.0)	5.0 (9)	(0.1-25.0)
% LOI	11.0 (13)	(3.3-17.0)	1.9 (9)	(0.3-5.4)
Oil & Grease	7610. (15)	(2900-24440)	870. (9)	(360-3550)

(N) = Number of Stations

5.0 CONCLUSION

One of the major objectives of the 1983 In-Place Pollutants Program was to obtain a good understanding of the relationship between contaminant levels in benthic organisms and those in the sediment that the organisms feed on. The data showed that such a relationship is a complex one, possibly involving various chemical, physico-chemical and physiological factors.

With regards to the uptake of contaminants by organisms, two trends were apparent. Several organochlorine pesticides were found at very low concentrations in sediment (many at the detection limits) but were elevated in benthic tissue at certain stations. Most of these stations were in the vicinity of storm sewers and sewage treatment plant discharges. Based on the results of other MOE studies (D. Boyd, 1987), indications are that low levels of these pesticides are discharged by these outfalls which provide the major source of uptake to benthic organisms. Once in contact with anaerobic sediment, these pesticides are readily degraded. The other trend is in relation to the other parameters, namely PCBs, Hg, Cu and Zn, which showed bioaccumulation. Here concentration by biota above sediment levels occurred in areas where the sediments had low organic matter content (measured as LOI, TOC, and SOL). There was no direct proportionality between the levels of these contaminants in sediment and benthic organisms and in the majority of cases, sediments with higher levels of these contaminants showed relatively low uptake by biota because of the correspondingly high levels of organic matter in these sediments.

The survival of benthic organisms in areas of relatively high levels of contamination and the concentration of certain contaminants in the tissue of these organisms raises concerns related to the potential for transfer of these contaminants to higher organisms that feed on these benthic species.

From a polluted sediment perspective, pesticides do not appear to be a major problem in contrast with urban storm sewers and sewage treatment

plant discharges. However, with regards to copper, zinc, PCBs and mercury, the sediments appear to be the major source of uptake by benthic organisms.

The sequential extraction procedure used in assessing the geochemical distribution of metals in sediment provides useful information on potential availability and the fraction(s) that influence body burden. The actual amounts of metals released from sediment may not necessarily be equivalent to the amounts potentially available because of physico-chemical factors and the amounts of organic matter in sediments.

Contaminated sediment is a source of contaminants to benthic organisms and can exert toxic influences on benthic organisms by completely eliminating benthic populations or reducing the diversity to a few tolerant species. The effects of continuing discharges such as storm sewers and STP discharges cannot however, be overlooked, since they are still of major concern in areas with contaminated sediment. Any management strategy to improve sediment quality must first address input from these sources.

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